THE STUDY OF CRYSTAL GROWTH
USING
THE ELECTRON MICROSCOPE

by

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N. G. A.

C O N T E N T S

I PREFACE

I. PREFACE

The nature of crystals as regular arrangements of molecules or atoms was early appreciated in the development of modern science. As long ago as 1784 Haüy suggested that simple geometrical solids such as cubes or spheres could be piled up in such a way as to reproduce many crystal forms. In this way the idea that crystals were regular arrangements of hypothetical building units was introduced into crystallography. The idea was later modified and extended by Bravais in 1850 when he formulated his space lattice theory in which Haüy's building units were replaced by particles regularly distributed in space to form a three-dimensional network or lattice. The possible types of space lattice were subsequently worked out mathematically and structures tentatively proposed for some crystals long before the advent of modern x-ray crystallography had confirmed the correctness of the theory. With the development of the techniques of x-ray investigation, quantitative determinations of crystal structure became possible so that to-day accurate and detailed knowledge is available concerning the distribution and arrangement of atoms and molecules within the crystals of an enormous rangeof substances.

Ideas concerning the way in which such regular arrangements of atoms or molecules could be built up from the random and chaotic distribution of the dispersed phased were, on the other hand, much slower in developing. Consequently, despite the advances made in the field in recent years as a result of the recognition of the importance of crystal

imperfections, many aspects of the problem still await clarification and many theoretical points are the subject of controversy.

The main reason for the slow development of crystal growth theory was the lack of methods of examining crystal surfaces either during growth or after growth had ceased. Consequently, the nature of crystal surfaces could only be speculated upon. It is true that in some exceptional cases where growth features of a coarser nature were present on crystal faces, some indications of the nature of the growth surfaces could be obtained, but again, owing to the lack of experimental techniques, their precise relationship to the atomic and molecular structure of crystal faces was uncertain and their interpretation was consequently somewhat difficult and subject to controversy. Fortunately, a number of experimental methods have now been evolved which have made possible the dirct examination of crystal surfaces. Firstly, the older light-microscope techniques have been considerably improved by the introduction of phase contrast which in favourable cases can reveal detail of molecular dimensions on crystal faces and by interferometric methods which are capable of determining the heights of such details. Secondly, an entirely new technique has been provided by the development of the electron microscope . Although the latter method is at present rather limited as the result of experimental difficulties which arise from the fact that entirely new techniques

have to be developed to produce specimens suitable for microscopy, it has been possible to study the surfaces of a number of crystals which lend themselves readily to this method of investigation. Phase contrast and electron microscopy have proved to be largely complementary. The phase-contrast techniques may be used in cases where the crystals are at present not within the range of electron-microscope techniques, while, in cases where it can be applied, the resolving power of the electron microscope in a three-dimensional sense is superior to that of the phase-contrast microscope.

In the present work the electron-microscope method has been utilised to study the surface structure of crystals of a number of related compounds. This study has made it possible to elucidate some of the problems related to the growth process of these compounds and to evolve theories which may be of assistance in the solution of the general problems of crystal growth.

II INTRODUCTION

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A. HISTORICAL SURVEY OF CRYSTAL GROWTH THEORY

a) The Development of the Classical Theory

The first theory of crystal growth to gain general acceptance was that put forward by Curie in 1885. This theory sought primarily to explain the development of crystal habit and did not concern itself with the actual mechanism of growth. Crystal were likened to liquid droplets and it was supposed that the equilibrium form of a crystal was such that its total surface energy was a minimum. Unlike liquid droplets, crystals cannot undergo a change in shape to reach the equilibrium form but it was supposed that the corresponding process in a crystal was the transfer of a quantity of material to the solution from one face and the deposition of an equal quantity on another. In this way a crystal could change its shape until a configuration with a minimum surface energy was attained. The Curie theory lost favour, however , when Valeton (1915) showed that while surface energy had probably a considerable influence on the shapes of very minute crystals, the effect became negligible in macroscopic crystals. The realisation of this fact made it apparent that further developments in the field must depend upon a consideration of the process occuring at a growing crystal face. A theory based on such a consideration was put forward by Volmer in 1921 and gained fairly widespread acceptance.

Volmer (1921,1922) developed the concept introduced by Gibbs in 1878 that the growth of a crystal face is discontinuous and takes place by the spreading of discrete molecular layers over the face. An important factor in this process was believed to be the surface migration of adsorbed molecules. According to Volmer, when a molecule condenses on a crystal face it does not give up all its energy of evaporation, but retains a fraction of it which enables it to exist in a mobile state on the face. Experimental confirmation of this view later supplied by Volmer (1932). As a result of this phenomenon, a crystal in equilibrium with its vapour will have adsorbed layers of molecules which have freedom to move in two-dimensions, present on its faces . If the vapour now becomes supersaturated, the concentration of molecules in the adsorbed layer will increase above its equilibrium value and the layer may consequently be regarded as supersaturated. It follows that such a layer is the two-dimensional analogue of the supersaturated vapour in which liquid droplets form from three-dimensional nuclei. The latter process depends on the formation of so called critical nuclei which are of sufficient extent to have equal chances of further growth or re-evaporation. Nuclei which are smaller than the critical nucleus dimension will probably re-evaporate, while those of larger size are most likely to continue growing. Consequently, we may expect that in the two-dimensional adsorbed layer on a crystal face, supersaturation will lead to the formation of two dimensional critical nuclei.

Such a nucleus will either vanish, the molecules rejoining the adsorbed layer, or grow out rapidly to cover the whole face, thus giving rise to a new crystal layer. Once the latter process has occurred we must again await the formation of a second critical nucleus which will produce the succeeding crystal layer.

The theory developed by Volmer, and later by Brandes (1927), paid little attention to the atomic or molecular structure of crystal faces, but emphasised the thermodynamic aspect of the problem. Kossel (1927), on the other hand, was of the opinion that the atomic or molecular structure of crystal faces was the dominant factor in growth. He argued that a crystal face could be built up by the adding of molecules to positions on a face such as A in figure 1, i.e., by the repitition of simple steps. Such steps would constitute a minimum periodicity of growth and were termed "Wiederholbare Schritte" by Kossel. Like Volmer, Kossel considers that growth takes place plane by plane. The rate of growth of any plane depends on the probability of a lone atom finding a point of attachment on the surface of a complete plane. Once this has happened the new plane will spread out with great rapidity to cover the whole face.

The approach adopted by Stranski (1928) was very similar to Kossel's, in that he placed emphasis on the atomic structure of faces rather than on the thermodynamical aspects. While Kossel, however, denies that any synthesis of his theory with that of Volmer, is possible, Stranski's

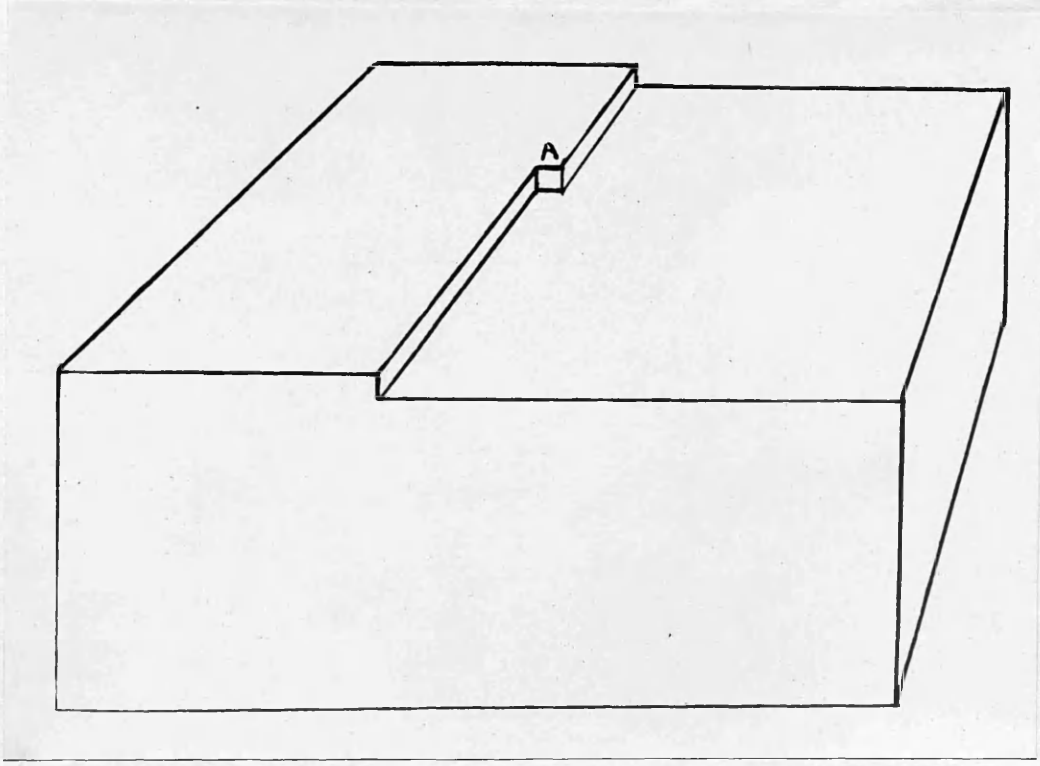

Figure 1. Diagrammatic representation of Kossel's 'wiederholbarer Schritt' concept. The step on the crystal face grows by addition of molecules to A, causing the 'kink' at this position to advance along the step.

view of the growth process is similar to Volmer's. From calculations of the work required to remove ions, ion pairs and groups of ions from the cube faces of rock salt crystals, he comes to the conclusion that there will be critical sizes of ion sheets and ion strips which can lose ions without themselves being dissolved. Once such sheets and strips have been formed on a face they will grow out rapidly to form a new crystal layer.

Becker and Döring (1935) adhere closely to Volmer's views. Like the latter their approach is mainly thermodynamical. They do, however, exclude the existence of an adsorbed layer and surface migration as important factors in the growth process. By developing the analogy of the formation of two-dimensional nuclei on a crystal face with the formation of three-dimensional nuclei in a supersaturated vapour they derive an expression for the rate of formation of nuclei very similar to equation (8) on page. 18.

The theories developed between 1921 and 1949, when Frank introduced his screw dislocation mechanism, may be said to belong to the classical period. All the theories of this period are based on (a) classical thermodynamics and (b) the classical concept of a perfect crystal. While some authors regard one or other of these approaches as the more important, at least one of these concepts is assumed in all the theories.

In 1949, in connection with certain discrepancies between experimental data and the classical theory which will be dealt with later, Burton, Cabrera and Frank undertook a re-examination of the classical theory. Their approach is essentially a synthesis of the theories of Volmer, Kossel,,Stranski, and Becker and Döring. Thus while considering growth as taking place by Volmer's surface nucleation process, they also recognise the importanc of 'kink' positions in steps (Kossel's wiederholbare Schritte). In the following section the approach to the classical theory is along similar lines to that adopted by these authors.

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b) THE RESULTS OF THE CLASSICAL THEORY

i) The Nature of a Growing Crystal Surface

According to the Volmer theory a face of a crystal growing from the vapour may have an 'island' nucleus present on it. This nucleus is in the process of rapidly growing out to form a new crystal layer. Let us imagine that during this process growth is suddenly arrested while the new layer is still incomplete and that equilibrium is set up between the crystal and its vapour. The surface will now have the features portrayed in figure 2. As well as the nucleus ABCD, there will be present a number of adsorbed molecules (E), double molecules (F), etc., the numbers of each molecular aggregate decreasing rapidly with the number of molecules present in it. There will also be a number of surface holes (G). Provided the temperature is above absolute zero, the edges AB, BC, etc., will not be straight, but will contain a number of molecular kinks. The latter act as exchange sites and the steps advance by addition of molecules to these kinks from the adsorbed layer. Burton, Cabrera and Frank (1951) have shown that the number of molecular spacings (x_o) between kinks is given by

$$x_o = a \exp(\phi/kT)/2$$

where ϕ is the energy of interaction between neighbouring molecules,

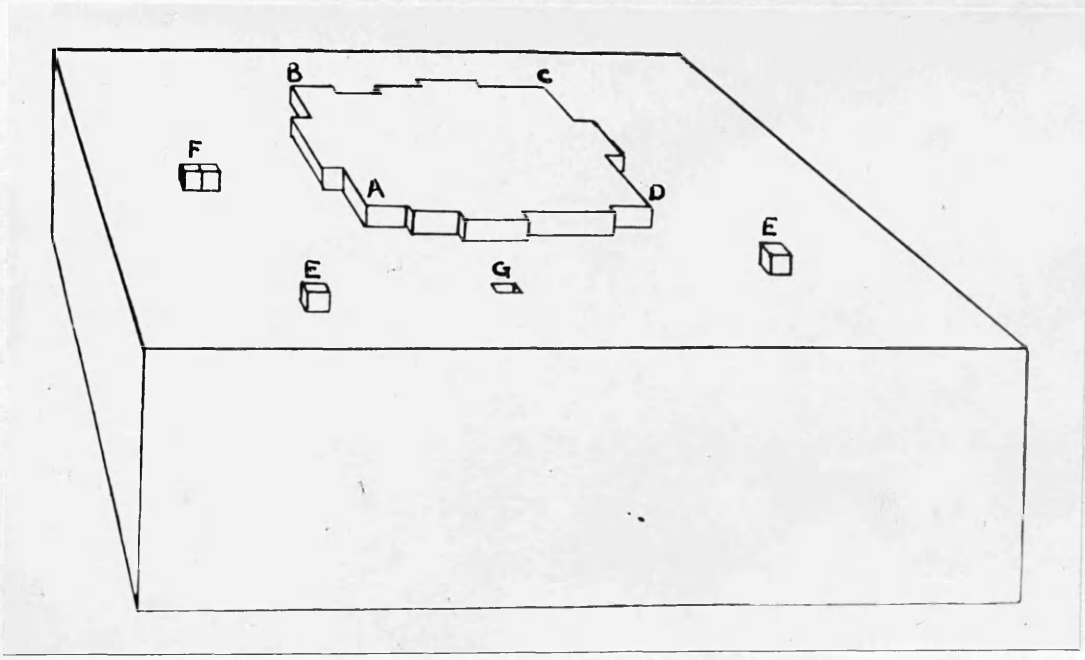

Figure 2. The nature of a growing crystal face according to the classical theory of crystal growth. ABCD represents a two dimensional nucleus, E an adsorbed molecule, F an absorbed double molecule, and G a surface hole.

Since ϕ/kT is usually about 4, there should be about one kink for every four molecules in a step parallel to a close-packed direction on the face of a typical crystal.

At equilibrium molecules enter and leave the kinks at equal rates. The rate at which molecules leave the kinks depends on temperature alone, while the rate at which they enter depends on the concentration in the adsorbed layer and consequently on the concentration of the vapour. If the vapour is supersaturated, the rate at which molecules join the kinks becomes greater than the rate at which they leave and the step advances.

ii) The Critical Nucleus.

If we now subject the crystal to a supersaturation the new layer will grow to completion. Further growth of the crystal now depends on the collisions between molecules in the adsorbed layer producing a two-dimensional nucleus of sufficient extent to survive . Such a nucleus is termed the critical nucleus, since it has an equal chance of growing out to form a new layer or re-evaporating.

The dimensions of the critical nucleus may be arrived at by considering the transfer of a small number of molecules from an infinitely large amount of material to the nucleus on a crystal face. The mole-

cules are first evaporated from the infinitely large mass at the equilibrium pressure, p_o, and compressed to the supersaturation pressure, p. In this process an amount of energy is used up which is equal to

$$- dn\, kT.\ln(p/p_o) - dn\,\lambda_v$$

where λ_v is the latent heat of evaporation per molecule. The molecules are then condensed onto the crystal surface with the liberation of an amount of energy $dn\lambda_a$, where λ_a is the latent heat of evaporation of a molecule in the adsorbed condition. They are then brought under the influence of the edge energy of the nucleus and absorbed by the nucleus, an amountof energy being gimen up which is given by

$$dn\,\lambda_n + 8\phi\, dr/2a$$

where a is the distance between nearest neighbours, λ_n the latent heat required to transfer a molecule from the nucleus to the adsorbed layer and r half the side of the critical nucleus which we may for the present consider as square. Since ϕ is the nearest neighbour interaction energy, $\phi/2$ is the edge energy per molecule in the edge and since 8r is equal to the perimeter of the nucleus, and 8r/a consequently the number of molecules in the edge, 8dr/a equals the change in the number of molecules in the edge when dn molecules are added to the edge. Hence the total change in free energy in the whole process is

$$dG = - dn\lambda_v - dn\, kT.\ln(p/p_o) + 8\phi\, dr/2a + dn\lambda_a + dn\lambda_n$$

But,

$$dn\,\lambda_v = dn\,\lambda_a + dn\,\lambda_n$$

Hence, denoting p/p_o, the supersaturation ratio, by α, we have

$$dG = -dn.kT.\ln\alpha + 8\phi\,dr/2a \qquad \ldots.(1)$$

The critical nucleus is, however, in unstable equilibrium with the vapour, and under these conditions $dG = 0$. Consequently, for the critical nucleus,

$$kT\,dn.\ln\alpha = 4\phi\,dr/a \qquad \ldots.(2)$$

Now, the area of the nucleus is $4r^2$ and if there are n molecules in it, the area is also $n\times a^2$, i.e.,

$$4r^2 = na^2 \qquad \ldots.(3)$$

Hence, $$n = 4r^2/a^2 \qquad \ldots.(3a)$$

and $$dn = 8rdr/a^2 \qquad \ldots.(3b)$$

Substituting in (2), we have

$$\frac{8rdr}{a^2}.kT.\ln\alpha = \frac{4\phi\,dr}{a}$$

$$r_c = a\phi/2kT.\ln\alpha \qquad \ldots.(4)$$

where r_c is the radius of the circle which can be inscribed in the square of the critical nucleus. r_c is loosely termed the radius of the critical nucleus.

iii) Rate of Formation of Nuclei.

The rate of formation of nuclei is important, since, assuming the Gibbs-Volmer theory is correct, it should enable us to calculate the rates of growth of crystal faces. For, provided the outward growth of nuclei once formed is extremely rapid, the number of layers added to the face in unit time should be equal

to the number of nuclei formed on the face in unit time.

According to general principles we should expect the rate of formation of nuclei to be equal to $\exp(-W/kT)$, where W is the work required to form the nucleus. Consequently, if we can find an expression for this work, we shall have a method of calculating this exponential From equation (1) we have

$$dG = - dn.kT\ln\alpha + 4\phi dr/a$$

Consequently the energy required to form a nucleus of n_c molecules and radius r_c is given by

$$G = -\int_0^{n_c} dn.kT\ln\alpha + \int_0^{r_c} 4\phi dr/a$$

$$= - n_c kT\ln\alpha + 4\phi r_c/a \quad \ldots\ldots(5)$$

But for the critical nucleus we have

$$r_c = a\phi/2kT\ln\alpha \quad \ldots\ldots(4)$$

Substituting for $kT.\ln\alpha$ in (5) we obtain

$$G = - n_c a\phi/2r_c + 4\phi r_c/a \quad \ldots\ldots(5a)$$

The number of molecules in the nucleus, n_c, is related to its radius, r_c, by equation (3a). Substituting for n_c in equation (5a), we have

$$G = -2\phi r_c/a + 4\phi r_c/a = 2\phi r_c/a \quad \ldots\ldots(6)$$

i.e., the energy required to form the critical nucleus is equal to half its edge free energy. By substituting the expression for r_c given in (4) in equation (6) we obtain

$$G = \frac{2\phi}{a} \times \frac{a\phi}{2kT\ln\alpha} = \frac{\phi^2}{kT.\ln\alpha} \quad \ldots\ldots(7)$$

This expression gives the work required to form the critical nucleus in terms of the energy of interaction between neighbouring molecules, which in simple cases is equal to $\frac{1}{6}$ the evaporation energy per molecule, the temperature and the supersaturation.

The rate of formation of nuclei (N) is consequently given by

$$N = A\exp\left\{-\phi^2/(kT)^2 \ln \alpha\right\} \qquad \ldots\ldots(8)$$

where A is a constant which can readily be seen to be equal to the number of molecules arriving at the surface per second. For the number of nuclei formed per second must be related to the number of molecules arriving at the surface per second. Not every molecules which strikes the surface, however, will give rise to a critical nucleus, but only a small fraction of these molecules and this fraction is determined by the exponential term.

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c) THE CLASSICAL THEORY AND EXPERIMENT

With a view to obtaining experimental verification of the surface nucleation theory, Volmer and Schultze (1931) undertook a study of the growth of crystal from their supersaturated vapours. The substances investigated were iodine, mercury and naphthalene. The apparatus used in the experiments is shown in figure 3. A large mass of the material was placed in one limb of the U-tube and a single crystal in the other. The U-tube was subsequently evacuated so that the crystals should be in contact with their vapour alone. During each experiment the limb containing the reservoir of the material was kept at 0°C, while the one containing the single crystal was kept at temperatures below this. The rate of growth of faces of the single crystal was observed at intervals by a microscopic method.

Volmer and Schultze believed that the results of these experiments had verified the predictions of the surface nucleation theory at least qualitatively and this view recieved fairly general acceptance for a considerable period. However, it was pointed out by Burton, Cabrera and Frank in 1949 that not only had the results not verified the theory, but had actually provided strong evidence against it.

The recognition of the divergence between the ex-

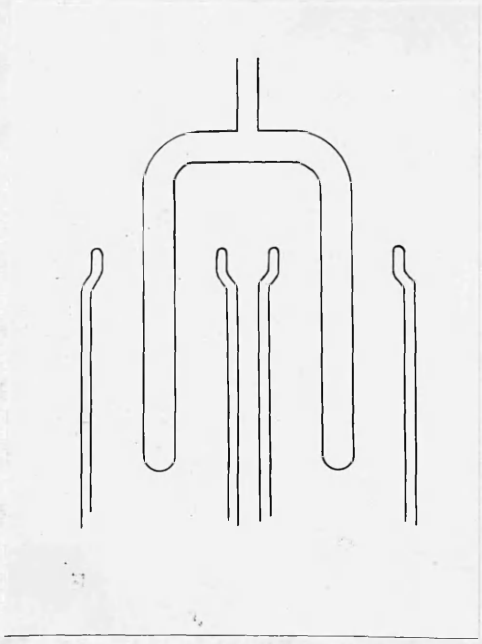

Figure 5. Diagrammatic representation of the apparatus used by Volmer for the study of the rates of growth of crystals.

perimental results and theory arose through an attempt to substitute the experimental data of Volmer and Schultze in equation (8). For a difference in temperature of 0.15° between the limbs of the U-tube , the highest rate of outward growth of a crystal face observed in the case of iodine was 0.019mm./hour . Using the value of 15 kcals per mole for the latent heat of sublimation of iodine and substituting in the approximate form of the Clapeyron-Clausius equation

$$\ln(p/p_o) = \ln\alpha = L.\Delta T/RT^2$$

we find that this temperature difference corresponds to a supersaturation ratio of 1.016. From the latent heat of sublimation per mole we obtain the latent heat of sublimation per molecule by dividing by Avogadro's number. Hence since $\phi = \lambda_s/6$, it follows that $\phi/kT = 4.6$. Thus the exponential factor in equation (8) is equal to

$$\exp(-21/0.016) = \exp(-1300)$$

In order to determine N we must obtain a value for A. This can be done simply by making use of the kinetic theory of gases . A cannot exceed the total number of molecules (n) striking unit area per second and this is related to the pressure (p) by the equation

$$p = 2nmu \qquad \ldots(9)$$

where m is the mass of a single molecule and u the average velocity per molecule.

For iodine,

$$m = 254/6\times10^{23} = 42.3\times10^{-23}$$

and u which can be taken with sufficient accuracy as the root mean square velocity, is given by

$$u = \sqrt{3p/d}$$

Taking the density (d) of iodine as 1.14×10^{-2} gm./cc., u is found to be 1.62×10^{4} cm./sec. at atmospheric pressure. At constant temperature this value should be practically independent of pressure so that we may use it in equation (9). Hence we have

$$n = \frac{p}{2mu} = \frac{3\times10^{-3}\times13.6\times981}{2\times42.3\times10^{-23}\times1.62\times10^{4}}$$

$$= 2.92\times10^{18} \text{ molecules/cm}^2\text{/sec.}$$

since the vapour pressure of iodine at 0°C is about 3×10^{-2} mm. of mercury. Thus for a surface of millimetric dimensions A will be of the order of 10^{16} mol./sec.. Substituting this value in equation (8) we obtain

$$N = 10^{16}\times e^{-1300} = 10^{-550}$$

Now, as already stated, the greatest observed rate of growth is 0.019mm./hour, i.e., 0.5×10^{-5} mm./sec.. Each layer is initiated by at least one nucleus and consequently the rate of formation of nuclei (N_o) cannot be less than

$$N_o = 0.5\times10^{-5}/10^{-7} = 0.5\times10^{2}$$

since the thickness of a layer is of the order of 10^{-7} mm..

Comparing this value with the theoretical value, we find that

$$\frac{N_o}{N} = \frac{0.5 \times 10^2}{10^{-550}} = 10^{550}$$

i.e., the observed rate exceeds the predicted value by the enormous factor of 10^{550}.

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d) BURTON AND CABRERA'S RE-EXAMINATION OF THE CLASSICAL THEORY

In the preceeding section we have seen that a discrepancy was found by Burton, Cabrera and Frank (1949) to exist between the predictions of the surface nucleation theory and the experimental observations. These authors found a rather larger discrepancy of e^{-3600}, but their approximations were rather cruder. Nevertheless, the value obtained in the last section makes it clear that the divergence between fact and theory is considerable. Furthermore, if we attempt to predict the supersaturation required to produce a perceptible rate of growth on the basis of equation (8), it becomes apparent that a supersaturation of at least 25% would be required. On the other hand, real crystals, as we have seen, grow at supersaturations of 1%.

In view of these inconsistencies, Burton and Cabrera (Burton, Cabrera and Frank, 1949, 1951) undertook a re-examination of the work of Becker and Döring. They found that the chief correction to be made in the theory lay in the shape of the critical nucleus. The importance of the latter can be appreciated from the following relatively elementary considerations.

As we have seen, Becker and Döring considered the case in which the nuclei were square. The radius of the circle which can be inscribed in the square of the crit-

ical nucleus is generally termed the radius of the critical nucleus. This quantity is related to the work required to form the critical nucleus by equation (6) :

$$G = 2\phi r_c / a = \frac{\phi}{2} \times \frac{4r_c}{a}$$

Since $8r_c$ is the perimeter of the nucleus, $8r_c/a$ is the number of molecules in the total edge of the nucleus. It follows that the energy required to form the nucleus is equal to one half of the total edge free energy (F) i.e.,

$$G = F/2 \qquad \ldots\ldots(10)$$

Consequently, equation (8) can be written in the form

$$N = A \exp(-F/2kT)$$

From this expression which is readily shown to be independent of the shape of the nucleus, it is apparent that, since the perimeter of the nucleus depends on its shape, the number of nuclei formed per second will also vary with the shape of the nucleus.

Now consider the shape of a circular nucleus. The number of molecules in the edge of such a nucleus will be $2\pi r_c/a$. It follows that

$$\frac{F'}{F} = \frac{2\pi r_c/a}{8r_c/a} = \frac{\pi}{4}$$

where F' is the edge free energy of a circular nucleus. Hence the edge free energy of a circular nucleus will be $\frac{\pi}{4}$ of the edge free energy of a square one and the edge free energy has thus a minimum value of $\frac{\pi F}{4}$. It

follows that the correction to the Becker and Döring expression cannot exceed a factor of $\frac{\pi}{4}$ in the exponential term. Burton and Cabrera find that the nucleus has a shape such that the correction factor has a value of 0.86 in the typical case. Hence the correction does not appreciably decrease the disagreement between the theoretical predictions and the experimental results.

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e) FRANK'S DISLOCATION MECHANISM

A way out of this theoretical impasse was subsequently suggested by Frank (Burton, Cabrera and Frank, 1949) He drew attention to the fact that studies of the strengths of solids had revealed that the strengths of real crystals were considerably smaller than those predicted for perfect crystals. This observation had led to the realisation that real crystals were imperfect and to the postulation of a number of imperfections to account for the observed strengths of crystals. The essence of Frank's suggestion lay in the recognition that one of these imperfections, viz., the screw dislocation, might play an important role in crystal growth.

Two main types of imperfection, known as the edge dislocation (Taylor, 1934) and the screw dislocation (Burgers, 1939), are believed to play a fundamental part in crystal plasticity. The nature of these dislocations can be readily understood by comparing a section of a crystal lattice which contains one of these dislocations with the ideal crystal lattice. In the perfect lattice we may mark out a complete circuit ABCDA (figure 4a). If we now attempt to trace out an identical path around a dislocation of the edge type (figure 4b), we find that the path no longer closes on itself. This path is represented by ABCDA' in the figure. The path difference A'A is known as the Burgers vector of the dislocation.

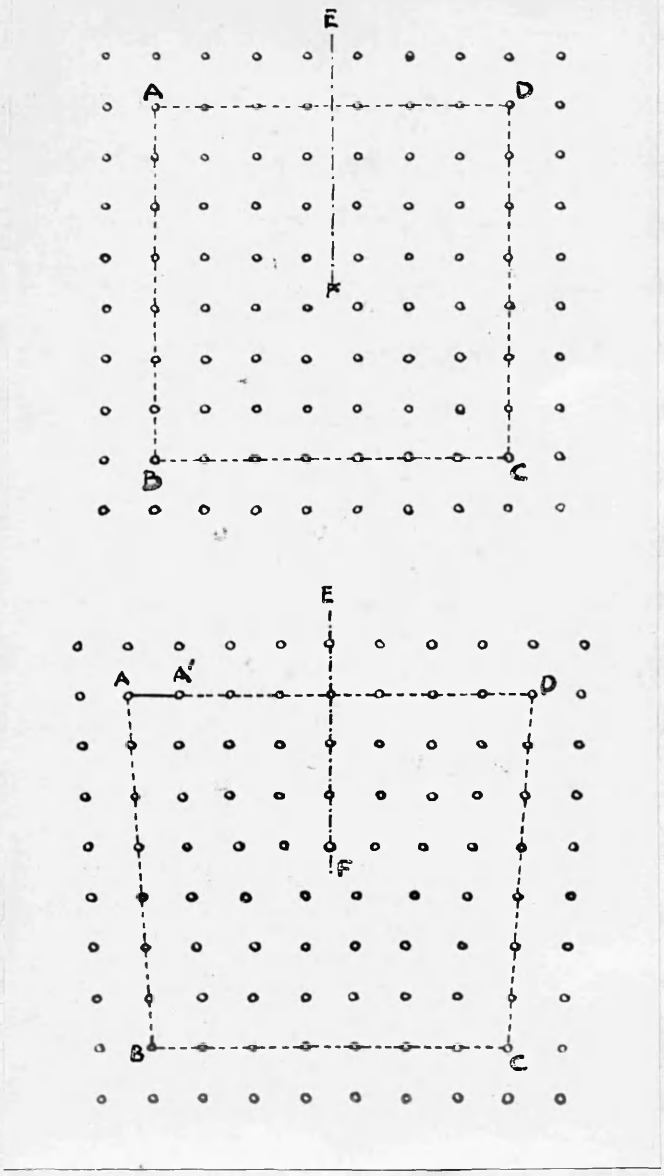


Figure 4. a) An ideal lattice in which the Burgers circuit ABCDA closes on itself.

b) A lattice containing an edge dislocation. In this case the Burgers circuit ABCDA' does not close on itself.

This type of dislocation can be imagined to arise in the manner depicted in figure 4(a) and (b) where the crystal is cut along the line EF and an extra layer of atoms inserted in the cut. There is a line of discontinuity running through F perpendicular to the plane of the paper. Along this line the atoms do not have their usual number of nearest neighbours. This line is termed the dislocationlline and by reference to figure 4(b) it will be seen that, in the case of the edge dislocation, the Burgers vector is perpendicular to the dislocation line.

The formation of a screw dislocation may be represented as shown in figure 5(a) and (b). An imaginary cut is made in a crystal along the section ABCD and the crystal on one side of it is displaced upwards with respect to the other side. There is then a line of discontinuity running through the point B perpendicular to the crystal face . We may again trace out a circuit in the ideal lattice which is denoted by abcdea in figure 5(a), and compare it with the corresponding circuit abcdea' in the dislocated lattice. In this case the Burgers vector turns out to be parallel to the dislocation line. The screw dislocation differs from the edge dislocation in the direction of its Burgers vector with respect to the dislocation line. It will also be noted that no extra layers of atoms are required for the formation of a screw dislocation.

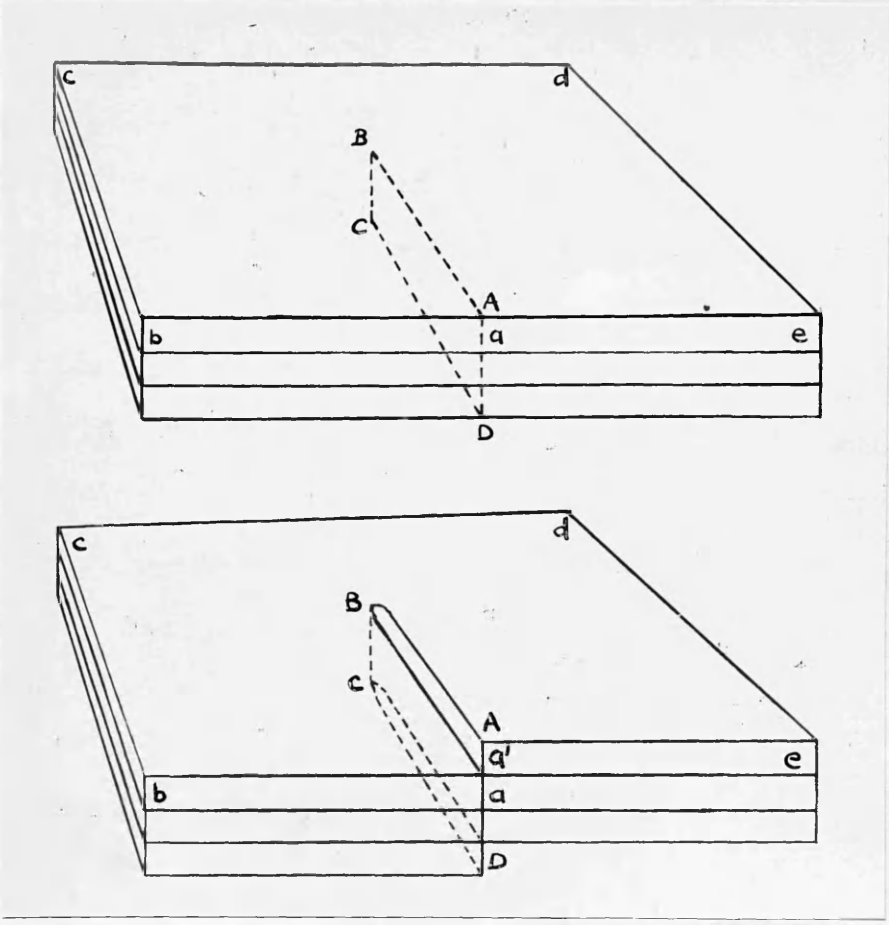


Figure 5. The formation of a screw dislocation in a crystal :

(a) Perfect crystal. In this case the Burgers circuit abcdea closes on itself.

(b) Crystal containing a screw dislocation. The Burgers circuit abcdea' does not close on itself.

It will have been noted in figure 5(b) that when a screw dislocation emerges on a crystal face it gives rise to a step running from the dislocation line to the edge of the face . If we now place such a crystal in its supersaturated vapour or solution , molecules will add to the step AB from the dispersed phase . The step, however, cannot be eliminated by growth . Condensation of molecules on it merely causes it to rotate around the dislocation centre. The reason for this is that the elimination of the step would mean the elimination of the dislocation. ,This cannot be done by growth, however, but only by reversing the process depicted in figure 5(a) and(b). Thus one end of the step must remain anchored at the dislocation centre and the step cannot grow out along its entire length to the boundary of the face, as is the case with a two-dimensional nucleus.

With continued growth the step originating from a screw dislocation does not remain straight, but winds itself into a spiral. This is due to the fact that the rate of advance of the step must be the same at all points along its length . The inner part of it, however, has a much shorter distance to travel to complete a circuit than the outer part. Points on the step near the centre are consequently able to complete several revolutions in the time that is necessary for the outermost points to complete a single revolution. Continuation of the process which is represented in figure 6(a), (b) and (c) inevitably produces a spiral

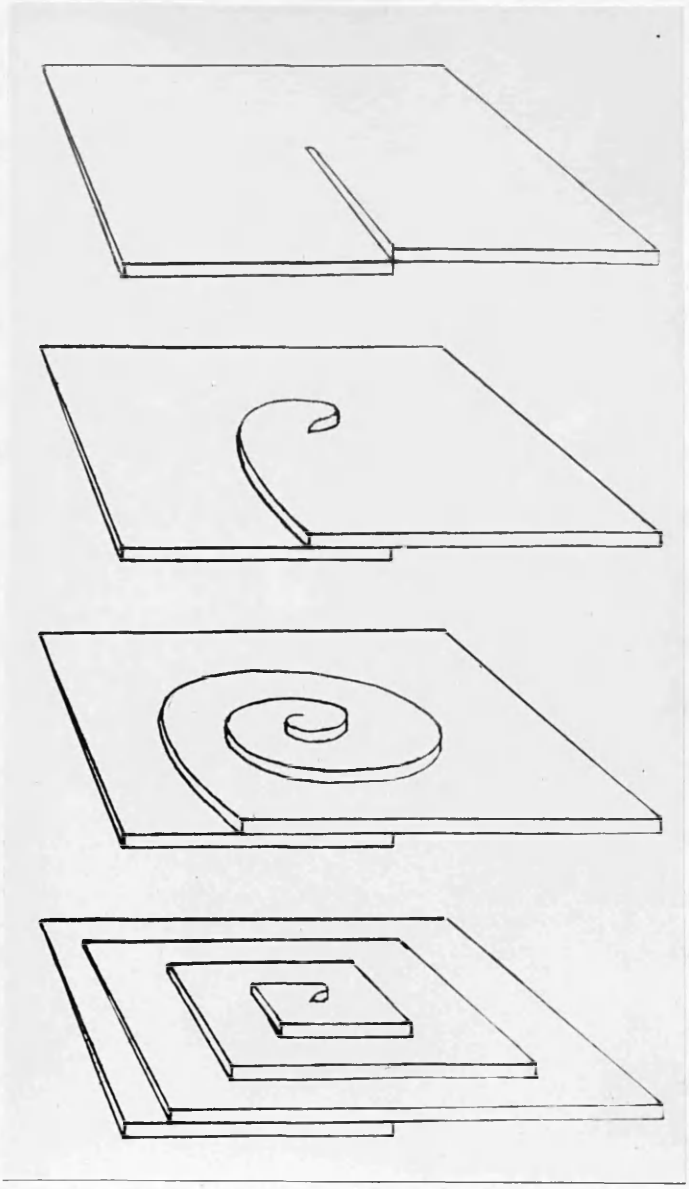


Figure 6. The development of a growth spiral on a crystal face:

(a) Step arising from a screw dislocation;
(b) and (c) Growth of the step leading to the formation of a spiral;
(d) Rectilinear spiral resulting from the disappearance of non - close-packed edges.

step.

The spirals formed by this process may be smooth curves, as shown in figure 6(c). Very often, however, the step edges will tend to follow close-packed lattice directions and the spirals will become rectilinear. This is in accordance with the well-known tendency of high-index (non - closed-packed) faces to grow extremely rapidly compared with those of low-index, with the result that only the latter are eventually present on the crystal. In the same way, the high-index edges present in a spiral of circular symmetry would be expected to disappear by rapid growth leaving only low-index edges. This process is represented by figured 6(c) and (d).

Referring again to figure 5(b) it will be appreciated that a crystal containing a screw dislocation does not, unlike an ideal crystal, consist of a large number of atomic layers placed one on top of the other, but is in essence a single layer wound into a helicoid structure. The thickness of this layer is determined by the magnitude of the Burgers vector of the dislocation. The helix formed by this crystal layer may be either right-handed or left-handed. Two screw dislocations may thus be identical in Burgers vector but differ in the sense of the helix formed by them. For instances, we could have obtained a dislocation from the crystal in figure 5(a) equal and opposite in sense to that in figure 5(b) by giving the dislocation a Burgers vector $-a'a$. If two dislocations

of opposite sense emerge on a crystal face, they give rise to two steps which rotate around their respective dislocation lines in opposite directions. Continued growth of the steps to form spirals is accompanied by the interaction of thesuccessive turns of the spirals in the manner shown in figure 7(a), (b) and (c). This process eventually gives rise to a series of closed loops spreading out from the two dislocation centres asdepicted in figure 7(d).

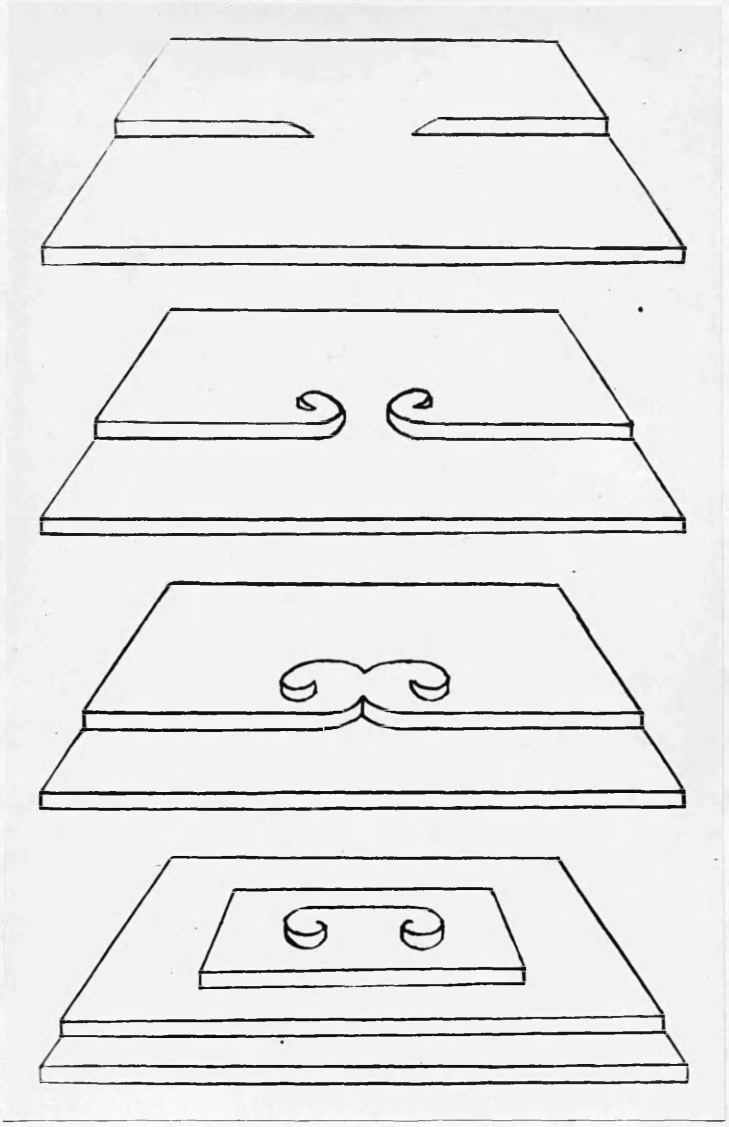


Figure 7. The developement of a closed-loop growth pattern;
(a) Two steps on a crystal face arising from two dislocations of opposite sense;
(b) and (c) The interaction of the two growth spirals;,
(d) The resulting closed-loop pattern.

f) EXPERIMENTAL VERIFICATION OF THE DISLOCATION THEORY

i) Experimental Observation of Growth Spirals.

After Frank had proposed the dislocation mechanism for crystal growth, the need was felt for further experimental confirmation of the theory. The most conclusive source of such evidence was to be sought in the direct examination of crystal surfaces, but at first sight the prospects in this field could not have seemed very bright, since it was expected that the Frank mechanism would give rise to steps of unimolecular height. However, abundant experimental observations of multimolecular steps on crystal faces were already available. Marcelin (1918) and Kowarski (1935), for instance, observed extremely thin steps on crystals of m-toluidine, and Volmer (1922) observed similar steps on lead iodide crystals formed by mixing solutions of lead nitrate and potassium iodide. Bunn and Emmett (1949) had described the observation of multimolecular growth steps on crystals of a large number of substances during the years 1932-49. In the case of carborundum crystals spiral markings had, in fact, already been observed (Menzies and Sloat, 1929; Lemmlein, 1947), but the authors had not realised the true significance of these and their work remained unnoticed for some time after the dislocation theory was introduced.

Experimental confirmation of Frank's theory was provided almost immediately by Griffin's (1950) study of the surface of beryl crystals. It was found that steps of high visibility were present on the $\{10\bar{1}0\}$ faces of these crystals and could, in fact, be observed by ordinary light-microscope methods. These steps were in many cases of the spiral form and besides simple spirals, systems of closed loops originating from two dislocations of opposite sense were observed. By making use of the method of multiple-beam interferometry (Tolansky, 1948) it was found possible to measure the step height. In one case this was calculated as 8.5± 1 Å. In other cases it was not possible to measure the step heights with accuracy but since there was no kink in the Fizeau fringes when they crossed a step line it was clear that they must be less than 20 Å high. Since the diameter of the Si_6O_{18} units is known from x-ray studies to be 7.9 Å it seems probable that the steps are of unimolecular height.

Further unexpected and striking confirmation of the screw dislocation theory of growth was provided by the electron-microscope study of crystals of the long-chain hydrocarbon n-hexatriacontane (Dawson and Vand, 1951). Micrographs of these crystals revealed the presence of growth steps which formed either simple spirals or the various combinations of spirals expected on the basis of the theory. It was possible to calculate the heights of the steps from the lengths of the shadows cast by

metal shadowing (Williams and Wyckoff, 1946) to which the specimens had been subjected in the course of preparation. The value obtained was 43 ± 5 Å and since the x-ray measurements had indicated that the molecular length was 48 Å it was thus established that the steps were unimolecular.

Since the appearence of these early results a considerable amount of evidence of the presence of spiral growth steps on the crystals of a wide variety of substances has accumulated. These results are summarised in table I. The results have been obtained by both light-optical methods and electron-microscope investigations. The light methods used have included ordinary microscopy in cases where the steps were of high visibility, and phase-contrast studies where the steps were finer. These methods have been combined with multiple-beam interferometry (Tolansky, 1948) in order to obtain estimates of the heights of the steps observed. A full description of the application of interferometric techniques to the measurement of step heights has been given by Verma(1953).

The crystals on which spiral growth steps have been observed belong to several different chemical classes and include metals, elements, and various inorganic and organic compounds. Consequently the nature of the crystals differs widely, some being heteropolar, e.g.,

TABLE I

Substance	Author	Source of Crystals	Step Heights	Method of Observation
1. Metals.				
Cadmium	Forty(1952d)	Grown from vapour	UM	LM
Gold	Amelinckx (1952f)	Chemical precipitation	MM	LM
Magnesium	Forty(1952c, 1952d)	Grown from vapour	UM	LM
Silver	Forty and Frank(1953)	Grown from vapour	UM	LM
Titanium	Steinberg (1952)	Grown electro-lytically	MM	LM
2. Elements				
Graphite	Horn(1952)	Natural	MM	LM
Platinum	Votava (1953)	Chemical precipitation	MM	LM
3. Inorganic Compounds				
Aluminium boride	Horn, Fulham Kasper(1952)		MM	LM
Apatite	Amelinckx (1952c,d)	Natural	UM	LM
Beryl	Griffin (1950, 1951a,b)	Natural	UM	LM
Biotite	Amelinckx (1952g,h)	Natural	UM	LM
Cadmium iodide	Forty(1951, 1952a,b)	Grown from solution	MM	LM
Haematite	Verma(1952c, 1952d)	Natural	MM	LM
Lead iodide	Forty(1952)	Grown from solution	--	LM
Mica	Amelinckx (1952g,i)	Natural	MM	LM
Pot. Ferro-cyanide	Amelinckx + Votava(1953)	Aqueous solution	MM	LM
Pyrites	Seager(1952)	Natural	MM	LM
Quartz	Willis(1952)	Natural	MM	LM
	Weill(1952)	Natural	MM	LM
Silicon carbide	Verma(1951a, b,c,d,1952a,b) Amelinckx (1951ab,1952ab)	Si+C	MM	LM

Substance	Author	Source of Crystals	Step Heights	Method of Observation
4. Organic Compounds				
Acids (benzoic, phenyl-acetic, suberic)	Brandstätter (1952, 1953)	Grown from vapour	MM	LM
Amides	"	"	"	"
Aromatic amines	"	"	"	"
Aromatic hydrocarbons	"	"	"	"
Camphor derivatives	"	"	"	"
Fatty acids:				
stearic	Verma and Reynolds (1953)	Benzene solution	UM, BM, TM, etc.	LM
behenic	Amelinckx (1953c)	Benzene solution	BM	LM
Long-chain alcohols	"	"	BM	LM
Long-chain hydrocarbons:				
n-Hectane	Dawson (1952)	Xylene solution	UM	EM
n-hexatri-acontane	Dawson and Vand (1951)	Pet. ether solution	UM	EM
Naphtha-lene derivatives	Brandstätter	Grown from vapour	MM	LM
Salol	Amelinckx (1952e, 1953a,b)	Benzene, EtOH, CCl_4.	MM	LM
Thymol	Votava, Amelinckx, Dekeyser (1953)	CCl_4, CS_2 solution and melt	MM	LM

Abbreviations: BM = bimolecular, LM = light microscope, MM = multimolecular, TM = trimolecular, UM = unimolecular.

cadmium iodide, and others homopolar, e.g., the long-chain paraffins and metals such as gold. This in turn has meant that the crystals studied have had a wide variety of internal structures.

The sources of the crystals were also extremely varied. Some were obtained by crystallisation in the laboratory, e.g., the long-chain paraffins, cadmium iodide and the metals cadmium and magnesium. Others were precipitated from solution by chemical means, e.g., gold. A further group was comprised of crystals derived from mineral sources, e.g., quartz, apatite, biotite, graphite, haematite, etc.. Two other sources of crystals are represented by silicon carbide and titanium. The crystals of the former may be described as synthetic since they arise during the preparation of the substances from the vapour. The vapour, however, is not that of silicon carbide, and its exact chemical constitution is unknown. The crystals of titanium examined by Steinberg (1952) are also synthetic since they were grown electrolytically. The observations thus refer to crystals formed under a wide variety of conditions.

ii) Step Heights.

From table I it will be noted that the step heights observed diverge considerably from the theoretical anticipations. In the majority of cases cited the steps are of multimolecular height, a fact to which they often owe their visibility. In some cases these large step heights may not be 'characteristic' of the substances in question.

In the case of gold, for example, it has been suggested by DeBlock (see Amelinckx, 1952f) that the crystals grow by epitaxy on sodium chloride crystals, along with which they are formed. Consequently the spirals observed may, in fact, represent spirals of large dislocation vector which may have been present on the substrate on which growth took place. However, it is clear that on many crystals spiral growth steps of multimolecular dimensions are present.

Of particular interest from the point of view of the present work are the observations which have been made by light-microscope methods on the long-chain fatty acids. In a study of stearic acid grown from benzene, Verma and Reynolds (1953) found from interferometric measurements that the steps were of heights equal to the x-ray repeat unit which corresponds to twice the molecular length, and to integrals of this value. They also found evidence of the presence of steps equal to odd integrals of half the x-ray repeat unit. More recently Amelinckx (1953c) has made a study of crystals of behenic acid, also crystallised from benzene and encountered only bimolecular steps.

The question of step heights has presented some theoretical difficulty. In view of the great strain surrounding dislocations of Burgers vectors equal to many molecular units, their occurrence in crystals would seem extremely unlikely. Frank (1951), in reviewing

the observations on silicon carbide, has suggested a process by which such dislocations could be produced. He refers to observations made in the investigation of the crystallisation of cadmium iodide. In the initial stages of growth from aqueous solution the formation of crystal sheets many molecules thick is observed. These sheets undergo rapid lateral growth until screw dislocations suddenly make their appearance. Frank supposes that as a result of the non-uniform distribution of impurities in the sheets, they undergo strain and buckling. This strain is subsequently relieved by large-scale crystal slip, which gives rise to dislocations of large Burgers vector.

iii) Polytypism

It has been suggested by a number of authors (Frank, 1951; Vand, 1951) that the presence of dislocations of multimolecular vectors may account for the polytypism which has long been known to exist in some crystals, e.g., silicon carbide and cadmium iodide. If two close-packed layers of atoms are stacked on top of one another, the atoms in the upper layer rest in the hollows formed between the atoms in the lower layer. If a third layer is placed on top of the second, there are two sets of hollows into which the atoms of this layer may fit. Thus the atoms in this layer may take up positions corresponding to those of the atoms of the initial layer, in which case the sequence may

be designated ABA . On the other hand, the atoms may fit into the other set of hollows, in which case the positions of the atoms do not coincide with those of the atoms in the first layer, and the sequence becomes ABC. The first of these structures occurs in the hexagonal close-packed crystals and the second in the cubic close-packed crystals, the layer sequences in these cases being ABABABABABAB.... and ABCABCABCABC...., respectively. In the polytypic substances various repeat units are found to occur and these units are generally more complex than in the simple hexagonal and cubic-close-packed cases. The repeat unit might, for example, be ABCACB. Now, if we consider a thick sheet of one of the polytypic substances, we may expect the sequence of layers to be random. Subsequent growth may lead to the formation of screw dislocations by the mechanism proposed by Frank. This will lead to a step of multimolecular height on the crystal face. The layer sequence present in this step will be perpetuated in the direction normal to the crystal face by the spiral growth mechanism. Hence the occurrence of the same layer sequence throughout a crystal which had previously presentdd considerable difficulty since it could not be explained on the basis of atomic interactions, was satisfactorily elucidated.

Evidence of polytypism has been observed by Verma (1951b, c, 1952a) in the growth spirals on carborundum crystals and

by Forty (1952a,b) in the growth spirals on cadmium iodide. In these crystals which have a hexagonal space lattice, cross-lacing is observed between adjacent steps at 60° to each other. Frank (1951) attributes this to variation in the rates of growth of the monolayers in different directions. Thus while one layer in a polytypic structure is the slowest-growing in one direction, causing the succeeding layers to pile up behind it, another layer may be the slowest-growing in the direction at 60° to the first. In the second direction the faster growing steps will pile up behind a different slow-growing step to those in the first. This feature causes the step to undergo branching on turning through 60° and to join two steps, not just one, in the succession of steps at 60° to the first.

Recently Amelinckx (1953c) has suggested that polytypism occurs in the long - chain alcohols and n-fatty acids. His view is based on light-microscopical examinations of the crystals of these substances which revealed cross-lacing between the spirals growth steps. He emphasises the similarity between the packing of the layers in alcohol crystals and that of the layers in hexagonal close-packed crystals, maintaining that the only essential difference is that the molecules are of rod-like form in the alcohols and not spheres, as in a close-packed metal. He then argues that layers piled up on top of one another may take up various positions corresponding to orientations of 0°, 60°, 120° and 180°. This interpretation has, however, been contested

by Anderson, Dawson and Watson (1954) who point out that interlacing may arise through a punch through of the spiral pattern on the lower face, a phenomenon which will be described later in this work.

iv) The Movement of Dislocations.

The modern theory of elasticity requires the presence of dislocations within crystals. The movement of these dislocations accounts for the fact that the strengths of materials are considerably less than those predicted for ideal crystals and for the plastic phenomena which are observed in solids. Since the emergence of a screw dislocation on a crystal face gives rise to a step of height equal to the Burgers vector of the dislocation extending from the dislocation centre to the edge of the crystal, the movement of the dislocation under an applied stress must raise a step on the surface of the crystal joining the new position of the dislocation centre to the original centre. Consequently, the movement of a dislocation might be expected to produce a recognisable effect on any growth features present on the surface of the crystal. In a study of silver crystals grown from the vapour, Forty and Frank (1953) have, indeed, found evidence of this type of phenomenon . Similar features to those observed when a dislocation has moved have also been observed in the present work, but as will become clear later, the observations are in this case better interpreted on the basis of internal slip.

g) GRAF'S LAMELLAR GROWTH THEORY

Besides the dislocation mechanism of crystal growth, one other theory has appeared in recent years. This is the lamellar growth theory put forward by Graf in 1951 to account for the occurrence of growth in thick sheets or lamellae on the crystals of a large number of substances. Graf considers that a crystal nucleus will remain a sphere as a result of the action of surface tension forces on it until it reaches a diameter at which its mechanical strength is just great enough to balance these forces. All the surfaces will then grow outwards except the closest-packed ones on which the potential hollows are too shallow to adsorb the highly mobile molecules arriving from the dispersed phase. If the crystal is of hexagonal symmetry, this means that the basal $(000\bar{1})$ and (0001) planes will not grow outwards and as a result of lateral growth of the nuclei flat lamellae will be formed. Furthermore, if growth takes place far removed from equilibrium the non - close-packed surfaces which form the edge of the lamellae will not become faces of low index. On the contrary, they will remain very irregular as the result of the growth conditions in which the addition of molecules will be faster than the rate of growth visualised by the 'tangential' growth of the Volmer and Kossel theories. When such a lamella has been formed, the surfaces of the closest-packed faces will be covered by mobile molecules. Collisions between these will lead

to the formation of a nucleus, and Graf argues that this will be spherical, rather than flat, again as the result of the surface tension forces. Such a nucleus must again grow until the mechanical strength is great enough to resist these forces. The nucleus can then undergo lateral growth leading to the formation of a second lamella on top of the first.

Graf makes no attempt to link his theory with Frank's dislocation mechanism, although it is apparent that a combination of the two theories could lead to an explanation of the observation of multimolecular steps on many crystals.

B. THE AIMS OF THE PRESENT WORK

As has been noted in the foregoing section, previous work on the long-chain hydrocarbons n-hexatriacontane (Dawson and Vand, 1951) and n-hectane (Dawson, 1952) had established that crystals of these compounds grow by the screw dislocation mechanism proposed by Frank (1949). The growth steps observed in these compounds were invariably unimolecular and no examples of multimolecular growth steps were encountered. On the other hand, numerous examples of crystals with dislocation centres consisting of two or more dislocations of the same sense were observed. These facts suggested that the height of the growth steps might be determined by the size of the molecular units present in solution.

Since the publication of this work, evidence of the occurrence of multimolecular growth steps on a large number of crystals has accumulated. In some cases, as, for example, gold (Amelinckx, 1952f) and silicon carbide (Verma, 1951a,b,c, d,1952a,b), it is unfortunately not possible to discuss the relation of step height to the size of the molecular units in the dispersed phase, since these crystals, being essentially synthetic , are formed from unknown molecular units or aggregates . Frank (1951) has attempted to account for the occurrence of multimolecular growth steps by supposing that the step height is determined by the strength of the parent dislocation. This conclusion is at variance with the original findings for the long-chain paraffins. Consequently, one of the aims of

the present investigation was to establish the exact relationship between step height and the size of the molecular units present in solution.

With this end in view representatives of the following series of compounds were chosen for study: the long-chain hydrocarbons with odd numbers of carbon atoms in their chains, the long-chain fatty acids and the dibasic carboxylic acids. These compounds were chosen for two reasons; firstly, because their known structures suggested that studies of their crystals might lead to some clarification of the step height problem and secondly, because their molecular lengths necessitated growth steps whose heights would give shadows within the limits of resolution of the electron microscope.

The structure of a hydrocarbon with a chain consisting of an odd number of carbon atoms was first examined in detail by Müller (1928) who found that n-nonacosane, $C_{29}H_{60}$, had an axial length equal to about twice the length of a single molecule. In contrast to this finding, the even n-paraffins were found to have an x-ray c-axial length approximating to the length of a single molecule. To account for this difference (Müller, 1929) postulated that the relationship between the terminal CH_3 groups must be the same in the crystals of both the odd and even paraffins. On this basis he was able to arrive at a fairly satisfactory explanation of the alternation in c-axial length. Figure 8 illustrates diagrammatically the structures proposed by Müller for the odd and

even paraffins and it will be apparent that the double-layer structure of the odd members could be perpetuated in a crystal by the presence of a dislocation of bimolecular strength, since in this case the crystal would really consist of a helicoidal double layer extending throughout the crystal.

Numerous investigations have been made on the n-fatty acids by both x-ray (e.g., Müller, 1927; Thibaud and Dupré la Tour, 1932) and by electron diffraction (Schoon, 1938) methods and it is now firmly established that the crystals consist of layers of double molecules stacked on top of one another. The molecules in the upper and lower halves of each layer are bound together by hydrogen bonding between the terminal -COOH groups. As in the case of the odd paraffins , such a layer structure could obviously be perpetuated in a crystal by means of a dislocation of bimolecular strength.

The fatty acids are also known to exist in at least two polymorphic forms which are designated the B and C forms, respectively. These modifications differ only in the tilt of the carbon chains with respect to the basal (001) planes. The structures may be considered as derived from that of the paraffins by tilting the chains towards the b-axis in the case of the B form and towards the a-axis in the case of the C form, the perpendicular distance between the chains being kept constant. The exact relationship between the polymorphic forms which occur in the fatty acids and other paraffin derivatives has been discussed by Schoon (1938, 1939).

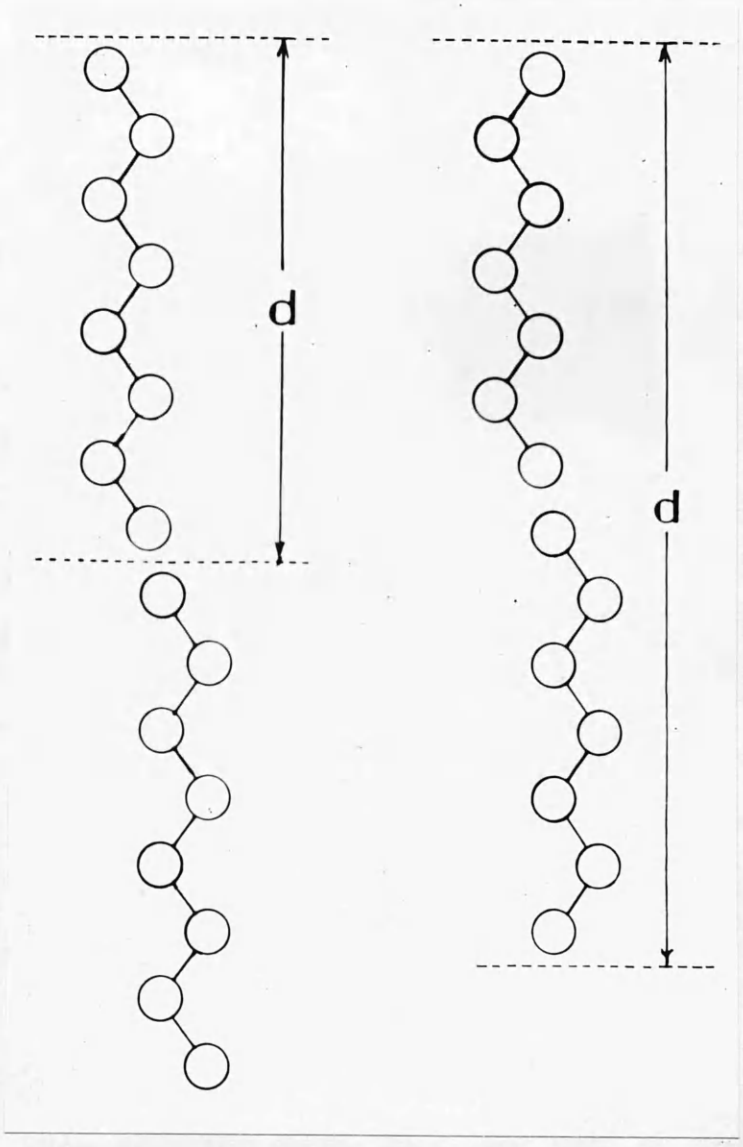


Figure 8. The relationship between the crystal structures of the even and odd members of the paraffin series.

The nature of the solutions of the fatty acids has been the subject of a number of investigations. Broughton (1934), for example, investigated their apparent molecular weights in cyclohexane by cryoscopic methods and his values for the freezing point depressions, in the case of palmitic acid, indicate that at a concentration of 0.0104 moles/litre the molecular association into double molecules may be as high as 79%. The degree of association is, however, not constant, but, as has been shown by Meisenheimer and Dorner (1936), varies with concentration and tends to zero at infinite dilution. Brocklesby, for instance, who studied solutions of the fatty acids in benzene by ebullioscopic methods, obtained boiling point elevations which indicate that the degree of dimerization of stearic acid rises from about 51% in a 0.026 molar solution to about 70% in a 0.154 molar solution. It therefore seems clear that the fatty acids exist to a considerable degree in the dimeric state in solution in non-polar solvents.

The cell dimensions of a series of dibasic acids have been determined by Caspari (1928). The results indicate that the unit cell is monoclinic and resembles that of the fatty acids, differing only in the tilt of the chains. Like the other paraffin derivatives the molecules are packed in layers. A study of sebacic acid (Morrison and Robertson, 1949) indicates that the molecules in successive layers are bound together by hydrogen bonding between their carboxyl groups. Since the molecules have carboxyl groups

at both ends, they form long chains extending through the crystals. Consequently, the structure is not a truely layered one, as in the case of the paraffins, since there is strong binding between the layers.

Little work appears to have been done on the nature of the solutions of the dicarboxylic acids. However, one would expect extensive association into chains in non-polar solvents, and little or no association in polar solvents. In the present work amyl acetate has been used as a solvent owing to the difficulties in preparing suitable crystals from other solvents. In this solvent one would expect little association between the acid molecules, although there may be some association with solvent molecules.

Spiral growth patterns have previously been observed on suberic acid, $HOOC.C_6H_{12}.COOH$, by Brandstätter (1955). The crystals examined were, however, prepared from the vapour.

The odd paraffins, the dicarboxylic acids, and the fatty acids, together with the paraffins of the even series, form a series in which we have :

(a) in the even paraffins, unimolecular units in solution and a unimolecular c-axial repeat unit in the solid state;

(b) in the odd paraffins, unimolecular units in solution and a bimolecular c-axial repeat unit in the solid state.

(c) in the dibasic acids, unimolecular units in solution and chains of molecules in th crystalline state;

(d) in the fatty acids, bimolecular units in solution and a bimolecular c-axial repeat unit in crystals.

It was hoped that an examination of this series would make it possible to assess the relative importance of dislocation vector, unit cell dimensions and molecular association in solution.

The study of the paraffins and their carboxylic acid derivatives were subsequently extended to include an examination of two-component paraffin mixtures and of the long-chain fatty acid esters, both of which have previously been found to exhibit interesting features.

The x-ray long spacings and melting points of paraffin mixtures have been determined by Piper, Chibnall and others (1931) with a view to finding methods of determining the purity of paraffins. They found that paraffins whose chain lengt did not differ by more than four carbon atoms formed mixed crystals for all composition ratios. The melting points of such mixtures lie on straight lines connecting the melting points of the pure paraffin components. Consequently the melting point of a mixture containing equal molecular proportions of $C_{26}H_{54}$ and $C_{28}H_{58}$ is the same as that of the $C_{27}H_{56}$. Furthermore, each mixture has its own definite

x-ray long spacing. For example, when $C_{28}H_{58}$ is added to $C_{26}H_{54}$ the x-ray long spacing rises continuously with increasing amount of the component with the longer chain. Rather unexpectedly, the long spacing becomes larger than that of $C_{28}H_{58}$ and continues to rise, reaching a maximum in the region of 97.5% of the component with the longer chain. Thereafter it falls to that of the pure paraffin $C_{28}H_{58}$. This behaviour was found to be general and is independent of whether both paraffins are even, both odd, or one odd and one even. In view of this it will be appreciated that the addition of one paraffin to another always leads initially to an increase in the x-ray long spacing independent of whether the contaminant has a longer or shorter chain than the paraffin to which it is added.

The esters of long-chain fatty acids were originally investigated as early as 1923 by Shearer who determined the long and side spacings of the methyl and ethyl esters of palmitic and stearic acid. Later a whole series of methyl and ethyl esters were examined by Malkin (1931). As a consequence of these studies it was recognised that the esters exist in at least two crystalline forms (Malkin, 1953). When the molten ester is cooled, the crystals formed have a structure in which the chains are perpendicular to the basal plane and in which the chains become hexagonally packed in the region of the melting point. This form is, in fact, analogous

in structure to the n-paraffins near their melting points. (Müller, 1932). This form has been designated the α-form. As the temperature decreases, the structure goes over to the β-modification in which the chains are tilted with respect to the basal plane. This form is analogous to the B-modification of the acids. The x-ray investigations have also shown that, when crystallised from alcohol and benzene (Francis, Collins and Piper, 1937) and from petroleum ether (Chibnall et al., 1934), the ethyl esters assume the β-form . Furthermore, Kohlhaas (1937) found that cetyl palmitate also crystallises from solution in the β-modification.

By the investigation of the surface structure of these derivatives of the long-chain hydrocarbons, viz., the acids and the esters, it was hoped that it might be possible to establish whether the chemical nature of the substance had any appreciably effect on the growth process. It is apparent from the above review of the previous knowledge of these compounds that the introduction of the polar carboxylic and ester groups has a marked effect on the crystalline modification of the acids and esters when compared with the simple paraffins. The exact origin of these differences in the crystalline state of these compounds is as yet unexplained. Furthermore, studies of the paraffin mixtures might reasonably be expected to yield information about the effect of contaminants on crystal growth.

III EXPERIMENTAL PART.

A. THE EXPERIMENTAL TECHNIQUES.

The study of organic crystals by electron microscope techniques presents special problems which are not generally encountered in the other fields where electron microscopy has found application. These problems arise from the chemical and physical properties of organic compounds and, in particular, the interaction between their molecules and the electron beam. In the present work some study has naturally had to be made of methods of overcoming these difficulties.

The best results are undoubtedly obtained by direct examination of the crystals of the substance to be investigated in the electron microscope. Direct microscopy has previously been employed in the investigation of n - hexatriacontane (Dawson & Vand, 1951) and of n - hectane (Dawson, 1952). In the present work it has been possible to employ this method for the study of n -nonatriacontane and n -propyl n-pentacontanoate (see section 111B). When the direct technique is adopted, the specimens are prepared by placing drops of a solution of suitable concentration on the specimen mounts which have previously been covered with a supporting film of formvar or nitrocellulose. The drops are allowed to evaporate and the suitability of the specimens for electron

microscopy judged by a preliminary examination in a light microscope. If suitable, the specimens are subsequently subjected to metal shadowing prior to examination in the electron microscope.

To permit of direct examination in the electron microscope a crystal must conform fairly rigidly to certain conditions. For this reason the method cannot be employed in the majority of cases. These conditions are as follows:

(a) the compound under investigation must be stable to electron bombardment. This, of course, necessitates that the substance be sufficiently high melting to withstand the heating effect of the electron beam. High melting point, however, does not in itself determine the stability of a substance to the impact of fast electrons. In many cases compounds, particularly of the aromatic class, appear to undergo decomposition on exposure to high-speed electrons. The aromatic compound periflanthene, for example, which does not melt below 483° C, is observed to decompose rapidly when examined in the electron microscope. On the other hand, the paraffin n-hexatriacontane which melts at 74.8° C is quite stable in an electron beam and may be examined without difficulty by the direct method. In view of these facts it is apparent that, in addition to melting point, molecular structure is of importance in deciding the suitability of a compound

for direct electron microscopy.

(b) The crystals must be extremely thin. This condition is imposed, firstly, by the necessity of limiting the heating effect due to electron scattering during observation. Secondly, since crystal growth studies are primarily concerned with the surface structure, the contribution of the layer of shadowing metal to the total scattering must be high compared with that of the crystal.

When these conditions are not fulfilled recourse has to be made to replica techniques.

In the course of the present work the relative merits of three replica techniques have been investigated, viz., those employing nitrocellulose or formvar, silicon monoxide and carbon as the replicating material. Of these three the nitrocellulose or formvar technique is the oldest and was originally used by Mahl (1940), by Mahl and Duffek (1942-3), by Zworykin and Ramberg (1941) and by Schaefer and Harker (1942) in the investigation of surfaces. The method was further developed by Williams and Wyckoff (1946) and its use in the study of virus crystals has been described by Wyckoff (1949). In the method developed by this author the specimens are first deposited on a glass slide and shadow-cast. A film of nitrocellulose or formvar is then formed on the slide by spreading a solution

of the plastic over its surface. When dry this film is floated off on to a water surface and picked up on specimen mounts. When the specimen consists of crystals, these are detached along with the film, as also is the layer of shadowing metal, and may be dissolved out by the application of a suitable solvent. A nitrocellulose replica of an aromatic hydrocarbon crystal prepared in this way is shown in figure 9, while the dicarboxylic acid crystals illustrated in figures 35 & 36 provide examples of formvar replicas. The method, however, is very restricted in its usefulness for dealing with organic crystals owing to the condition that the substance to be examined must be insoluble in the solvent used for the nitrocellulose or formvar.

Silicon monoxide has been frequently used for the preparation of replicas in the course of the present work. This method of preparing replicas which was used by Hall (1950) in an investigation of celestin crystals, has the advantage that no stripping or flotation is required. Much tearing and distortion is thus avoided. A small amount of silicon monoxide is placed in a molybdenum boat and evaporated *in vacuo* on to the specimens which have previously been deposited on specimen mounts and shadow-cast. In the study of crystals of stearic acid (section 111 C) the best results were obtained with 0.15 mgm. of

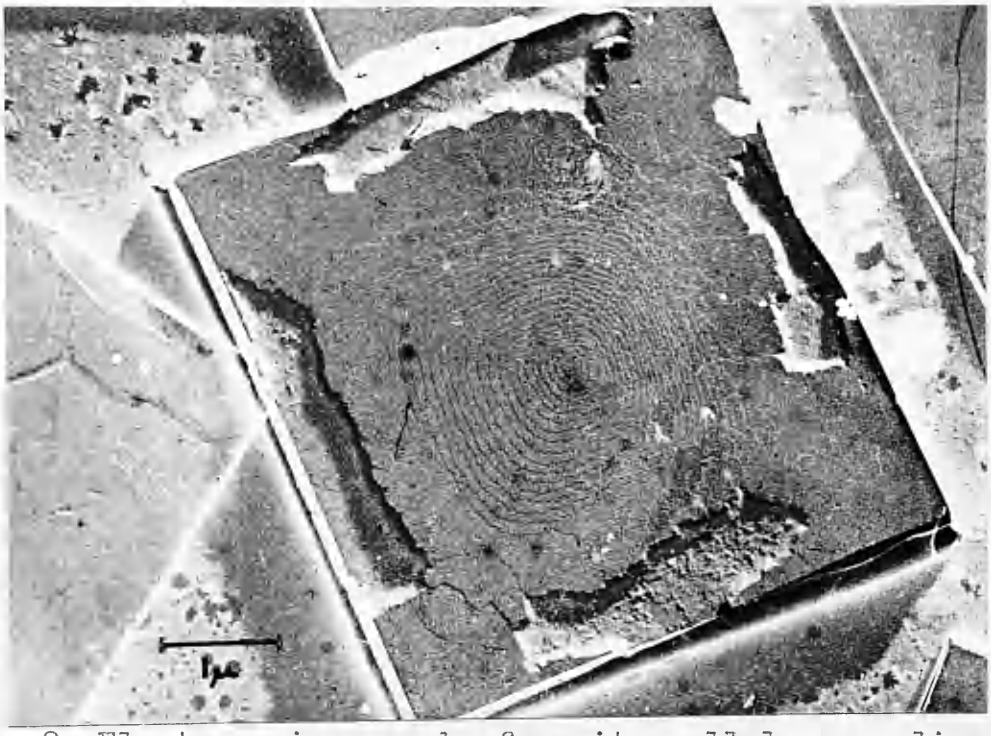


Figure 9. Electron micrograph of a nitrocellulose replica of a periflanthene crystal.

Figure 10. Electron micrograph of a silicon monoxide replica of a stearic acid crystal badly damaged by the replicating process

silicon monoxide in the boat for a filament-specimen distance of 9 cm. Both the crystals and the formvar supporting film are later extracted with a suitable solvent before examination in the electron microscope.

Despite the convenience of the silicon monoxide technique which is engendered in the *in situ* preparation of replicas, the method suffers from a serious disadvantage arising from the fact that there is considerable heat transfer from the filament to the specimens. The resultant heating of the specimens is apt to damage the crystals causing extensive melting. The seriousness of this feature is illustrated by figure 10 which shows a specimen of stearic acid which has undergone this type of destruction. Consequently, great care has to be exercised in the evaporation of the silicon monoxide. Damage to the specimen is reduced by keeping the filament dimensions as small as possible and by using a quantity of silicon monoxide which is just sufficient to give a stable film. Despite these precautions, however, the number of good replicas obtained in the case of stearic acid was small.

Frequently, difficulty is encountered in dissolving the crystals out of nitrocellulose (or formvar) and silicon monoxide replicas. This difficulty, however, was readily overcome in the case of the substances

studied in this work, by exposure to the reflux vapour of the solvent.

A further replica technique whose potentialities for the study of organic crystals were investigated in the course of the present work was that described by König (1951) for the preparation of carbon replicas. This method was adapted to the preparation replicas of stearic acid as follows. The crystals were first deposited on specimen mounts and shadow-cast in the usual manner. The mounts were then attached to one electrode of a high voltage discharge system and a discharge established in an atmosphere of benzene at a pressure of 1.5 m.m. of mercury. It was found that the desired thickness was attained when the discharge was continued for 1 minute at a current of 1.0amp. Before extracting the crystals from the replica it is necessary to harden the replica by exposure to the electron beam in the microscope, otherwise the specimens are liable to tear when treated with solvent or solvent vapour. A replica of a stearic acid crystal prepared by this procedure is shown in figure 11. However, the results are poor compared with those obtained by the silicon monoxide technique. A serious disadvantage arises from the necessity to harden the replicas by electron bombardment, since this process also hardens the formvar substrate, thus making it difficult to remove the

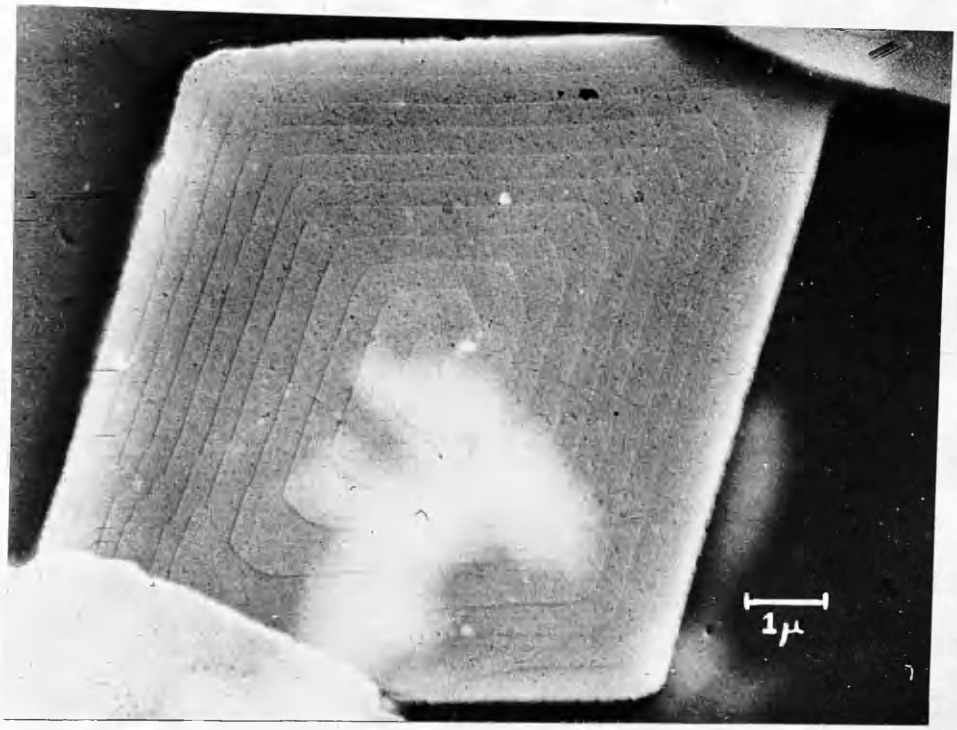


Figure 11. Electron micrograph of a carbon replica of a stearic acid crystal.

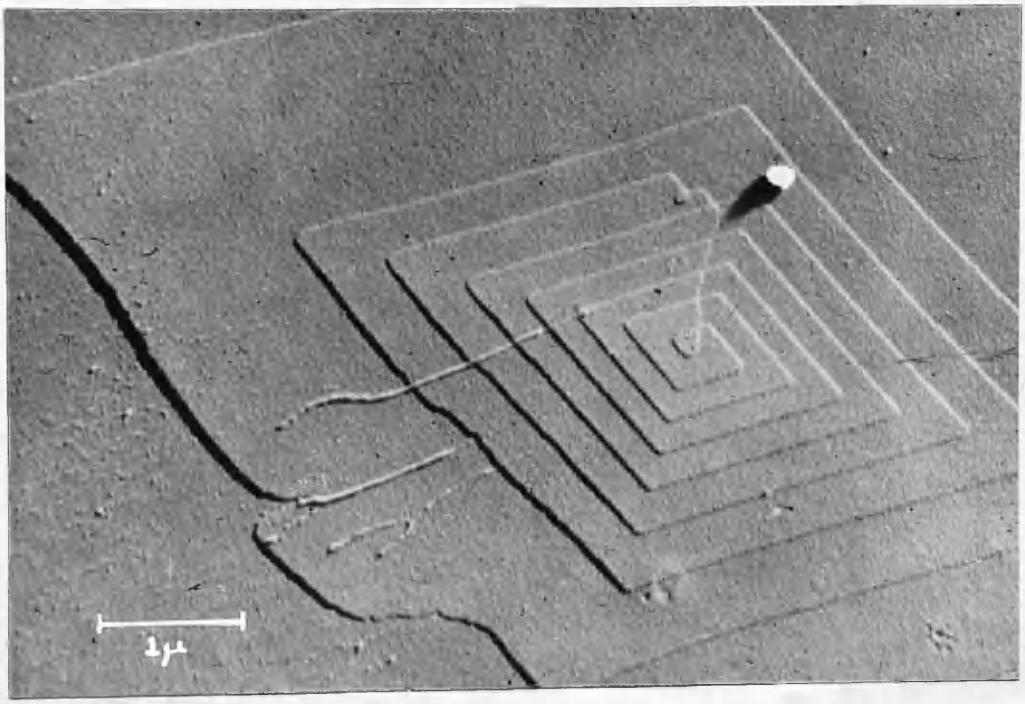


Figure 12. Electron micrograph of a heavily shadow-cast crystal of a paraffin mixture.

latter.

The nitrocellulose and silicon monoxide replica techniques are consequently the most suitable for the study of organic crystals and are largely complementary. The silicon monoxide technique, may, for instance, be used when the nitrocellulose method is excluded by solubility of the crystals in the solvent used for the nitrocellulose. On the other hand, it may be desirable to employ the nitrocellulose technique where the crystals are liable to be damaged by the silicon monoxide proceedure, or where it is necessary to deposit the crystals on a glass surface, as may happen when the solvent from which the crystals grow attacks formvar on nitrocellulose.
The two methods yield comparable results as will be seen from figures 33, 34 and 37, and figures 35 and 36, which show replicas of α dibasic acid in which silicon monoxide and formvar, respectively, have been used for replicating.

In some cases it is difficult to deposit the crystals on the specimen mounts, presumably because the solvent tends to run off onto the surrounding glass slide. In such cases crystals grow on the glass slide but not on the specimen mounts. This difficulty can often be overcome by forming a formvar film on a glass slide, depositing the crystals on it and floating it off onto

a water surface, where it is picked up on specimen mounts. This method has been used in the preparation of the dicarboxylic acid specimens illustrated in figures 33, 34 and 37.

Finally, it should be emphasized that artefacts must be carefully guarded against in the electron microscope study of crystals. This applies particulary to organic crystals which by reason of their fragile nature are extremely susceptible to damage by heat and electrons. Reference has already been made to the artefacts that may arise in the preparation of silicon monoxide replicas . Further artefacts may result from shadow-casting . Heavy shadowing, for example, frequently leads to exaggerated and variable step height valves. This is illustrated by figure 12 which shows a heavily shadowed crystal of a paraffin mixture. Examination of this micrograph shows that the steps near the crystal edge cast much longer shadows than those near the growth tip, although, since they all belong to the same growth spiral, they must all be of the same height. Step height measurements on such crystals will obviously lead to different values depending on the position at which measurement is made.

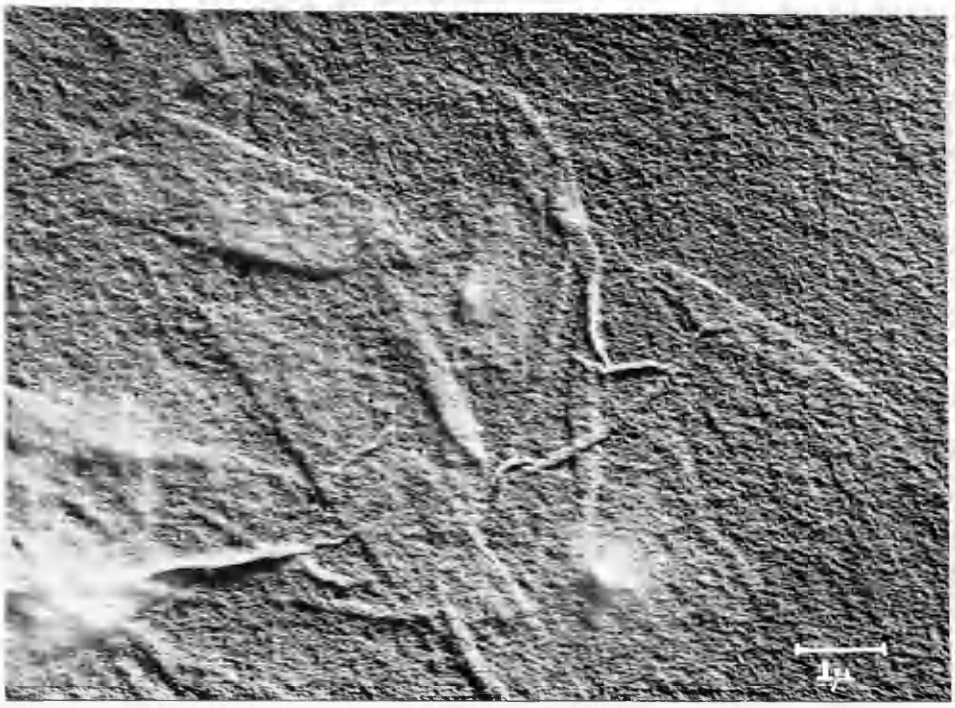


Figure 15. Electron micrograph of a specimen of the long-chain fatty acid ester n-propyl n-pentacontanoate prepared by crystallisation from alcohol on a formvar film. The crystalline material is completely obscured by an attefact due to the action of the solvent on the supporting film.

Solubility of the substrate in the solvent used for crystallisation may also be responsible for artefacts. Usually the supporting film undergoes complete rupture when this is the case. However, in some instances the effect is only one of partial solution , and an example of this is provided by figure 13. This micrograph shows the appearance of specimens prepared by crystallizing a fatty acid ester from ethyl alcohol on a formvar substrate. As a result of partial solubility of the substrate the presence of crystalline material is completely obscured.

B. MATERIALS AND METHODS.

a) MATERIALS AND SOURCES.

The member of the odd paraffin series chosen for study was n -nonatriacontane, $C_{39}H_{80}$ (m.p. 80.2°C), the synthesis of which has been described by Stenhagen and Tägtström (1944), to whom the author is indebted for the sample used. These authors determined the long spacing of the crystalline paraffin and obtained a value of 51.3 Å. In the study of paraffin mixtures this paraffin and n-hexatriacontane which was previously studied by Dawson and Vand (1951) were used. The fatty acid used in the investigation was stearic acid, $C_{17}H_{35}.COOH$ (m.p. 69.6°). The length of the c-axis of the C-modification of this acid was found by Müller (1927) to be 48.8A, i.e. nearly twice the length of the single molecule. This acid was followed by the dibasic acid hexadecane 1,16-dicarboxylic acid, $HOOC.C_{14}H_{32}COOH$ (m.p. 125.5°C). The sample used was prepared by Arosenius, Ställberg, Stenhagen and Tägtström (1948). The crystal structure of this acid has been investigated by Caspari(1928), who obtained a value of 25.10Å for the c-axis dimension. The series of compounds studied was completed by the long-chain ester n-propyl n-pentacontanoate, $C_{49}H_{99}.COOC_3H_7$ (m.p. 93.5°C), which was synthesised by Ställberg, Ställberg - Stenhagen, and Stenhagen (1952). These authors

These authors obtained a value of 70Å for the long crystal spacing.

b) SPECIMEN PREPARATION.

i) n-Nonatriacontane and mixtures of n-nonatriacontane and n-hexatriacontane.

Specimens of n-nonatriacontane were prepared in the manner already described by Dawson and Vand (1951) for n-hexatriacontane, i.e. by allowing drops of the solution in petroleum ether to evaporate on specimen mounts. The specimens were subsequently shadowed with palladium or nickel-palladium alloy and examined directly in the electron microscope.

The paraffin mixtures were prepared by direct weighing of the components. For this purpose a torsion balance weighing 1 mgm. was used. Mixtures containing $C_{38}H_{74}$ and $C_{39}H_{80}$ in the ratios 53.2% and 46.8%, 85.3% and 14.6%, and 21.4% and 78.6%, respectively, were prepared. A mixture whose precise composition was unknown was also investigated.

ii) Stearic Acid.

Crystals of stearic acid were grown both from petroleum ether and benzene. The crystals obtained from petroleum ether were deposited on specimen mounts in the

manner described for paraffins. They proved too thick for direct examination in the electron microscope and a replica technique had to be adopted. The most suitable was found to be the silicon monoxide technique described in the previous section (111A). The preparation of suitable crystals from benzene solution proved more difficult. Although suitable crystals are readily obtained on a cooled glass slide, the deposit obtained on nitrocellulose or formvar films is not crystalline in appearance. However, it was found possible to prepare suitable crystals in the following manner. A small amount of sodium ethoxide in alcohol solution (2c.c. of an approximately N/10 solution) was added 100 c.c. of a ½% solution of nitrocellulose in amyl acetate. A film was formed on a glass slide by spreading this mixture over it. After cooling the slide in a refrigerator, drops of the benzene solution of stearic acid were placed on the film and allowed to evaporate. This proceedure was found to give a fairly uniform distribution of small crystals over the areas covered by the drops. The effect of the presence of sodium ethoxide is apparently to prevent the droplets spreading over the nitrocellulose film as they usually do. The film containing sodium ethoxide is therefore similar to a glass surface on which droplets of benzene have no tendency to spread. The nitrocellulose film was subsequently floated off onto a water surface and picked

up on specimen mounts. The specimens were then shadowed and replicated with silicon monoxide in the usual manner.

iii) Hexadecane 1,16-Dicarboxylic Acid.

It was found that specimens of hexadecane 1,16 - dicarboxylic acid could be prepared by either of the following proceedures.

1) A glass slide is coated with formvar film and drops of a solution of the acid in amyl acetate placed on it. The film is floated off onto a water surface and picked up on specimen mounts. After drying, the specimens are shadowed with palladium at an angle of 10° and replicated by the silicon monoxide proceedure (111A). The crystals and the formvar substate are finally removed by exposure to the reflux vapour of ethylene dichloride.

2) The specimens are deposited on a glass slide, shadowed lightly with palladium, and replicated with formvar by the proceedure described in 111A. (The crystals of the acid do not appear to be appreciably affected by the solvent in the cold). The crystals were finally dissolved out by means of ether vapour. It was found advantageous to back the replicas with aluminium or silicon monoxide.

In some cases the specimens were damaged by the silicon monoxide proceedure despite the relatively high melting point of the acid. It was therefore thought advisable to prepare formvar replicas to check the results of the silicon monoxide method. Very similar results were, however, obtained by both methods.

iv) n-propyl n-pentacontanoate.

Specimens of n-propyl n-pentacontanoate were readily prepared by the method used for the preparation pf paraffin specimens. The ester was found to be rather too insoluble in petroleum ether at room temperature for the preparation of suitable specimens and it was necessary to dissolve the compound in the hot solvent and work with solutions somewhat above room temperature. A number of specimens were prepared by deposition on heated specimen mounts and a third group by allowing crystallization to take place before deposition on specimen mounts.

c) ELECTRON DIFFRACTION.

To supplement the information gained by direct microscopy the crystal structure of the specimens employed was investigated in the cases of n-nonatriacontane, the paraffin mixtures, stearic acid and n-propyl n-pentacontanoate by electron diffraction, for which

purpose the Philips electron microscope was used as a diffraction camera. The stearic acid specimens used for this purpose were, of course, not replicated but examined directly and although the specimens were generally too thick and unstable for direct microscopy, the crystals were quite stable at the low beam intensities used for electron diffraction. The ester specimens used for electron diffraction were crystallised from a higher boiling petroleum ether (b.p.100-120°) than that (b.p. 60-80°) used to prepare crystals for direct microscopy.

To obtain absolute measurements of the axial dimensions it was necessary to calibrate the microscope. For this purpose thallium chloride specimens prepared by subliming this substance onto specimen mounts *in vacuo*, were used. These specimens gave the usual powder patterns consisting of concentric rings and lattice constants corresponding to these rings were obtained from data given by the American Society for Testing Materials (1945). To avoid inaccuracies due to instability of the accelerating voltage and lens currents, a calibration pattern was taken after each crystal pattern without alteration of the instrument controls.

6) RESULTS.

a) n-NONATRIACONTANE.

i) Growth Patterns.

Examination of the specimens of n-nonatriacontane prepared by the method already described revealed the presence of very small lozenge-shaped crystals. On most of these clear evidence of spiral growth was observed and all the theoretically possible growth patterns were encountered e.g. simple spirals resulting from a single screw dislocation, multiple spirals originating from two or more dislocations of the same sense and closed loops arising from pairs of dislocations of opposite sense. As in the case of n-hexatriacontane the spirals were invariably of a rectilinear form.

ii) Step Height Measurements.

From measurements of the lengths of the shadows cast by the growth steps and the known angle of shadowing (15^{0}) a step height value of 45 ± 10 Å was calculated. In all, twenty three crystals were examined in detail and some two hundred steps measured. The value obtained corresponds within the limits of experimental error with the value of 51.3 Å calculated by Stenhagen and Tägtström (1944) for the molecular long spacing in crystals of paraffin. There

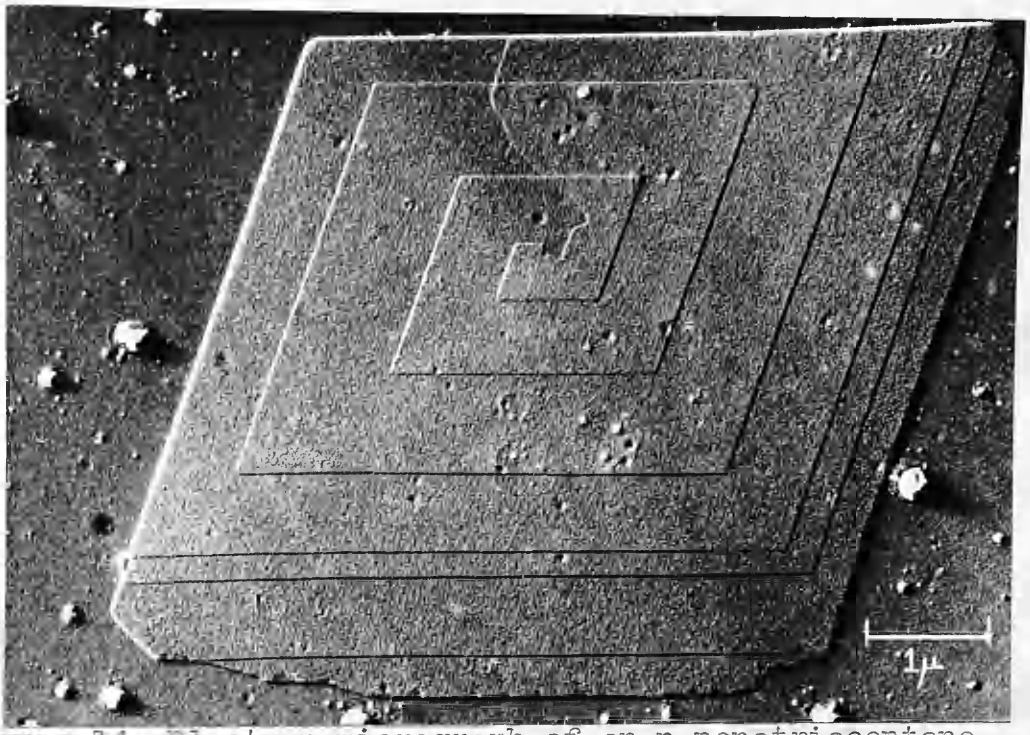


Figure 14. Electron micrograph of an n-nonatriacontane crystal showing a spiral growth step arising from a single dislocation. The step on the lower face has been rendered visible by the process of internal slip.

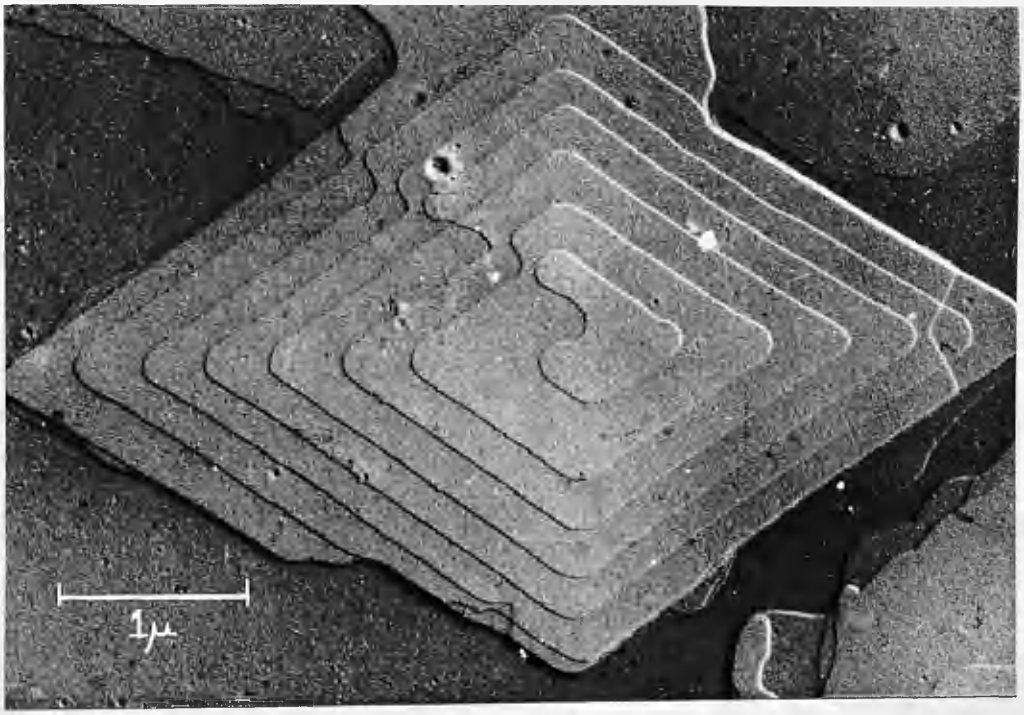


Figure 15. Electron micrograph of an n-nonatriacomtane crystal prepared by crystallisation 10-15° above room temperature. No evidence of dislocations is visible.

is thus little doubt that the steps are of unimolecular height.

No examples of multimolecular growth steps were encountered. Examples of two or more concentric spirals originating from multiple dislocation centres were, on the other hand, frequently observed.

iii) The internal Slip of Molecular Layers in Paraffin Crystals.

A striking feature of the micrographs of n-nonatriacontane crystals is the internal slip of the layers of paraffin molecules which takes place when a crystal settles on the supporting film prior to shadow-casting. When a crystal has a screw dislocation present in it, steps are necessarily present on both upper and lower faces of the crystal, and the face on which the crystal comes to rest is consequently not planar. The slip which takes place on settling is such as to render the lower surface planar and takes the form of faulting along the lines of the steps on this surface. Steps are thus induced on the upper face which correspond to those originally present on the lower, and these, together with the steps which were initially present on this face, are thrown into relief by shadow-casting. In this way the steps on both the upper and lower faces may be visible in

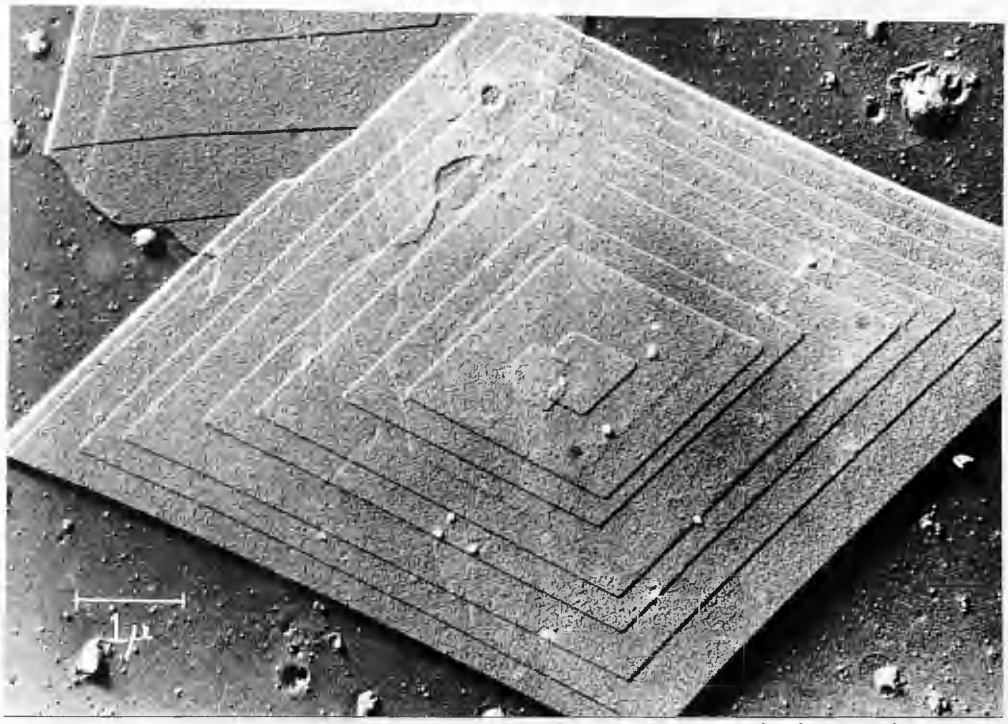


Figure 16. Electron micrograph of an n-nonatriacontane crystalshowing two central dislocations of opposite sense. The step joining the two dislocation centres on the lower face has been rendered visible.

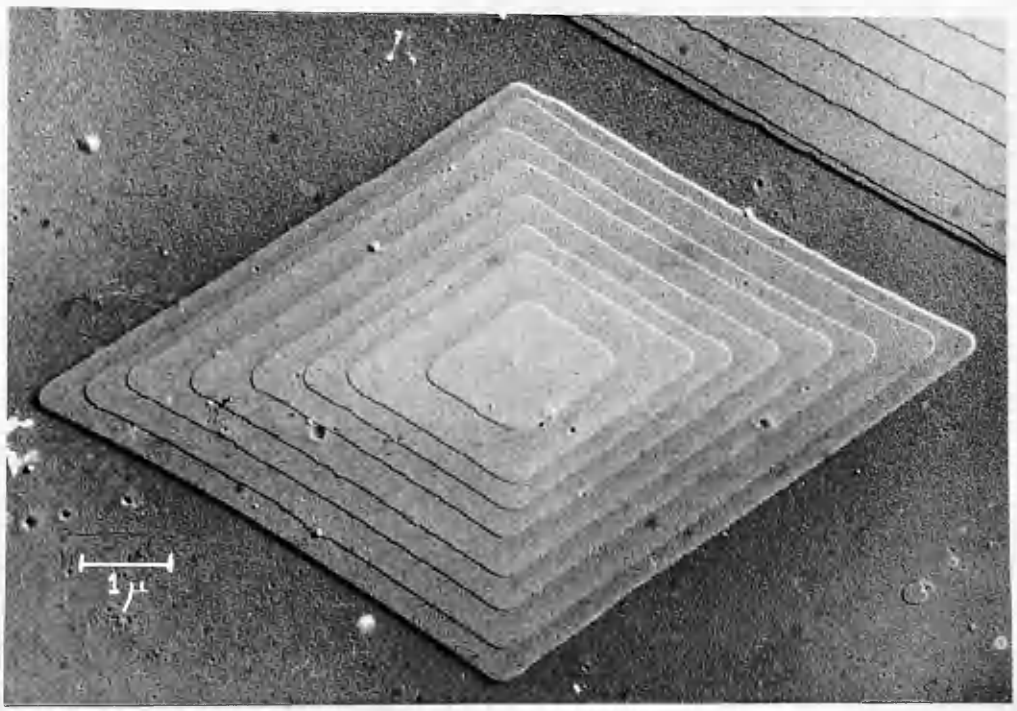


Figure 17. Electron micrograph of an n-nonatriacontane crystal. This crystal is related to that in figure 16 in the same way as the one in figure 15 is related to the one in figure 14.

a micrograph. This is illustrated by figures 14 and 16 where the lower step patterns which are very simple in nature, are visible in their entirety.

This effect is particularly noticeable in crystals of n-nonatriacontane which tend on the whole to be thinner than those formed by homologuous paraffins n-hexatriacontane and n-hectane. Even in the case of these latter paraffins, however, evidence of this type of slip is apparent in some micrographs.

A clear illustration of slip is provided by figure 19. In this example a thin sheet of n-nonatriacontane has been deposited on a growing crystal of n-nonatriacontane and, on settling, has taken up the contours of the growth steps of the crystal. A small amount of growth has occurred after this collapse and consequently the growth steps in the two halves of the picture were no longer in register when growth ceased.

The transmission of the lower growth patterns through the crystals does not generally occur in thick crystals. Figures 20 and 21, for instance do not reveal any details of the growth features on the lower crystal face.

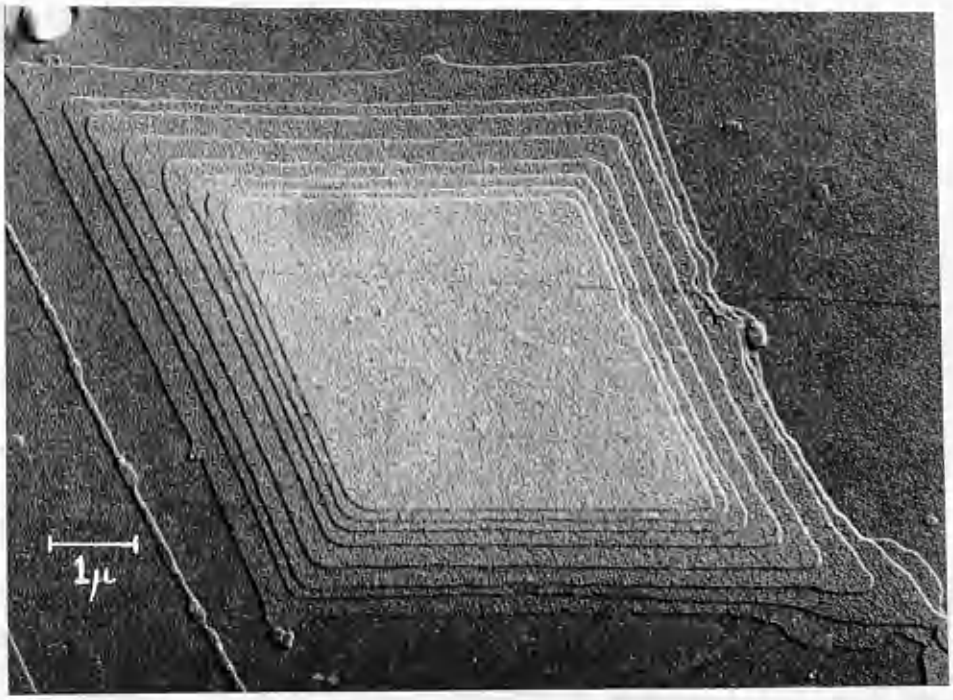


Figure 18. Electron micrograph of an n-nonatriacontane crystal. This crystal represents a later stage in the growth of a crystal of the type shown in figure 17

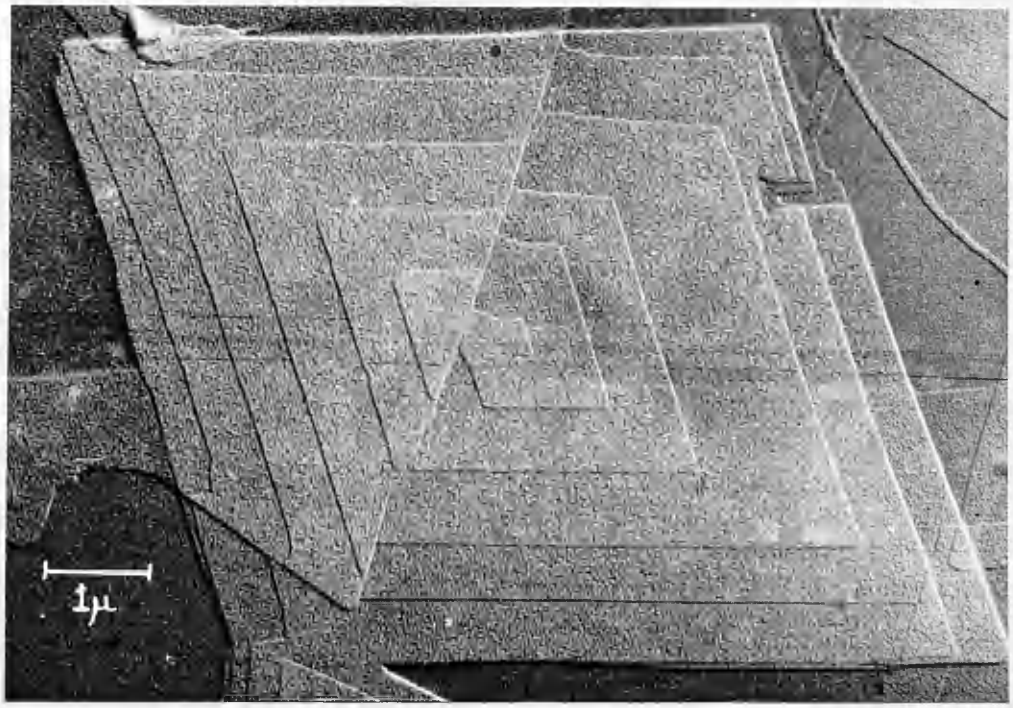


Figure 19. Electron micrograph of an n-nonatriacontane crystal. A monolayer has been deposited on the crystal and has collapsed along the lines of the steps on the underlying crystal.

iv) The Effect of Impurities on the Growth Step Pattern.

The micrograph shown in figure 21 provides a good example of the interference of a small dust particle with the growth pattern. Each growth step which has passed the particle is seen to be kinked in a position corresponding to that of the particle. Although some recovery by filling up of the kinks does take place, it is apparently a comparatively slow process and is incomplete by the time the steps have reached the edge of the crystal. A similar effect has been observed by Griffin (1951b) in the case of beryl.

Figure 19 is an interesting example of what might called "self-interference". The "impurity", in this case, a layer of paraffin of different orientation to that of the underlying crystal, has given rise to a series of growth steps of different growth rate to those on the original crystal. A study of the overlying layer thickness to the left of the micrograph would suggest that this layer is in fact of unimolecular thickness. There is a continuous boundary of alternately unimolecular and bimolecular thickness along the edge. It follows that growth has proceeded further and possibly faster on the steps created in the

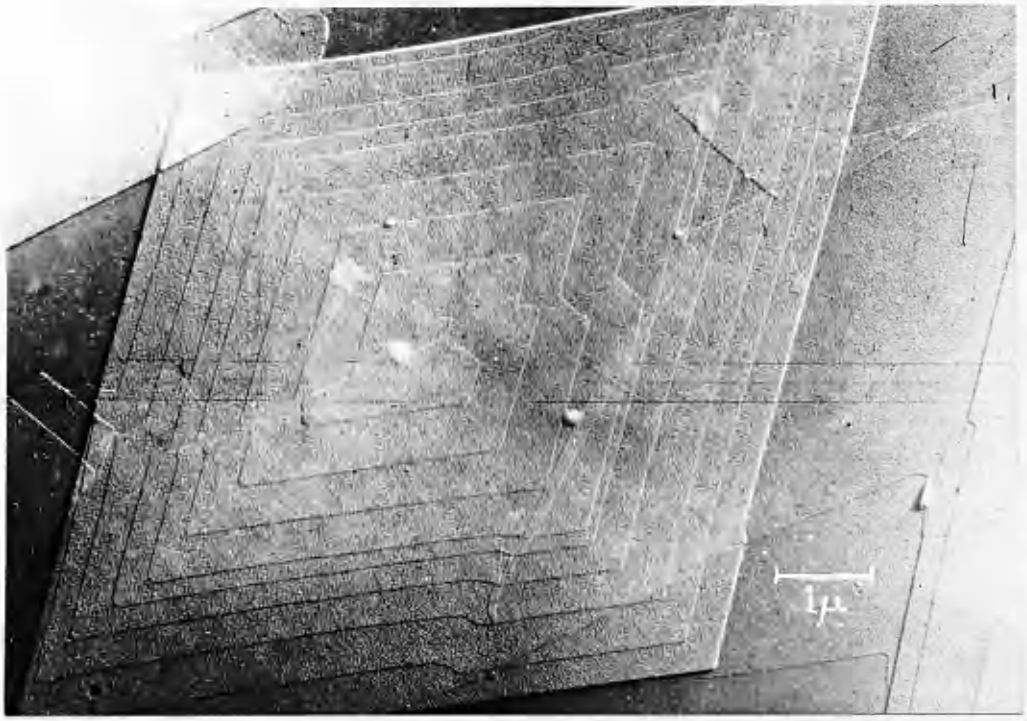


Figure 20. Electron micrograph of an n-nonatriacontane crystal in which there has originally been two dislocations of the same sense, one of which has been cancelled.

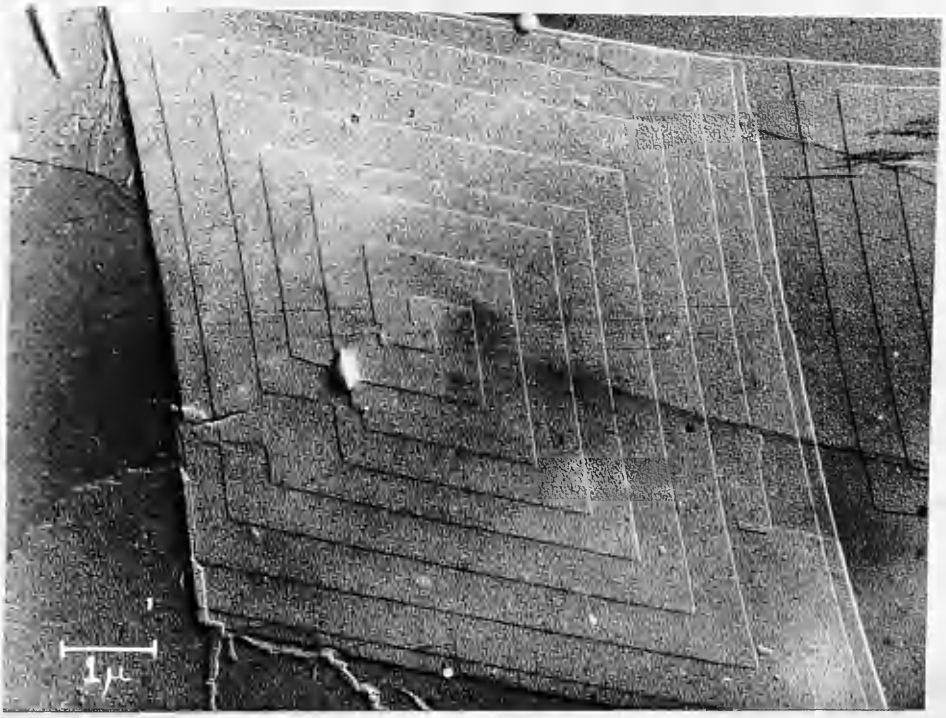


Figure 21. Electron micrograph of an n-nonatriacontane crystal. The dirt particle near the centre has given rise to a series of kinks in the steps.

overlying layer than in the pre-existing crystal steps. If growth were not faster on the step edges of the superimposed layer one would see a boundary consisting alternately of unimolecular steps and plane regions such as exist in figure 15. The rounded corners in the step edges on the overlying layer are confirmatory evidence of the faster rate of growth on this side of the micrograph.

The reason for the faster rate of growth of the steps on the superimposed layer is probably the difference in orientation. As a result the steps in this layer are not close-packed and tend to grow rapidly. Re-orientation of the steps to take up close-packed directions would appear to be comparatively slow.

v) Variations of Growth Pattern with Temperature.

Crystals of n-nonatriacontane grown by evaporation of solutions at room temperatures show the normal spiral growth patterns observed by Dawson and Vand (1951) in the case of n-hexatriacontane. Examples of crystals showing this characteristic growth form are provided by figures 14 and 16, the crystals in these micrographs differing from those observed in n-hexatriacontane only in the fact that, in addition to the spiral growth pattern on the

upper face, the pattern on the lower face has been rendered visible by the process of internal slip already described. In figure 14 the lower pattern consists simply of a step joining the dislocation centre to the periphery of the crystal. This is, in fact, the step produced by the dislocation on the lower face of the crystal, which unlike the one of the upper face, has not developed into a spiral. In figure 16, on the other hand, the pattern consists of a single step joining two dislocation centres of opposite sense. These results suggest that the crystals have grown while in contact with the substrate film, so that the transport of molecules to the lower face has been effectively prevented, with the result that the spiral patterns have only developed on the upper face.

Crystals of n-nonatriacontane prepared by evaporation 10° to 15°C above room temperature show a different type of growth pattern which is illustrated by figures 15 and 17. These patterns are of particular interest since they show no immediate evidence of spiral growth. On the contrary, they consist of closed loops and, unlike the closed loop patterns originating from the interaction of two dislocations of opposite sense, show no evidence of dislocations at the growth tip. This type of pattern is, in fact, somewhat misleading since

it would at first sight indicate a growth mechanism similar to that visualised by the Gibbs-Volmer theory. For the interpretation of this type of growth pattern it is important to notice the succession of kinks in the growth steps which are seen along a line joining the apex to the periphery of the crystal illustrated in figure 15. This particular example is characteristic of many crystals of n-nonatriacontane which have this type of growth pattern.

v) The Crystalline Modification of the n-Nonatriacontane Specimens

Electron diffraction measurements on crystals of n-nonatriacontane showed that these were invariably of the orthorhombic modification of the paraffin with the following unit cell dimensions : $a=7.45 \pm 0.04$ Å and $b=4.95 \pm 0.02$ Å. No examples of the monoclinic form reported by Stenhagen and Tägtström (1944) were encountered.

b) MIXTURES OF n-NONATRIACONTANE AND n-HEXATRIACONTANE.

i) Growth Patterns.

As is the case of the pure paraffin n-nonatriacontane, electron microscope examination of paraffin mixtures revealed the presence of very small crystals which exhibited spiral growth steps on their surfaces. In contrast to the pure paraffins, however, the growth centres were sometimes very complex. This is illustrated by figure 22 where about ten distinct dislocation centres can be recognised at the growth centre. In addition to this, the crystal slip already described seems to be more common than in the pure paraffins.

ii) Step Heights.

A series of 18 crystals of a paraffin mixture containing 21% $C_{36}H_{74}$ and 79% $C_{39}H_{80}$ were subjected to accurate step height measurements and a value of 52$\pm$ 3Å was obtained. It thus appears certain that the steps on these crystals are unimolecular. Detailed examinations of this kind were not made on crystals of the other paraffin mixtures, but a number of measurements indicated that the steps on these were also unimolecular. There is therefore little doubt that the steps on paraffin crystals are unimolecular, independent of whether the crystals consist of the pure paraffins or are mixtures.

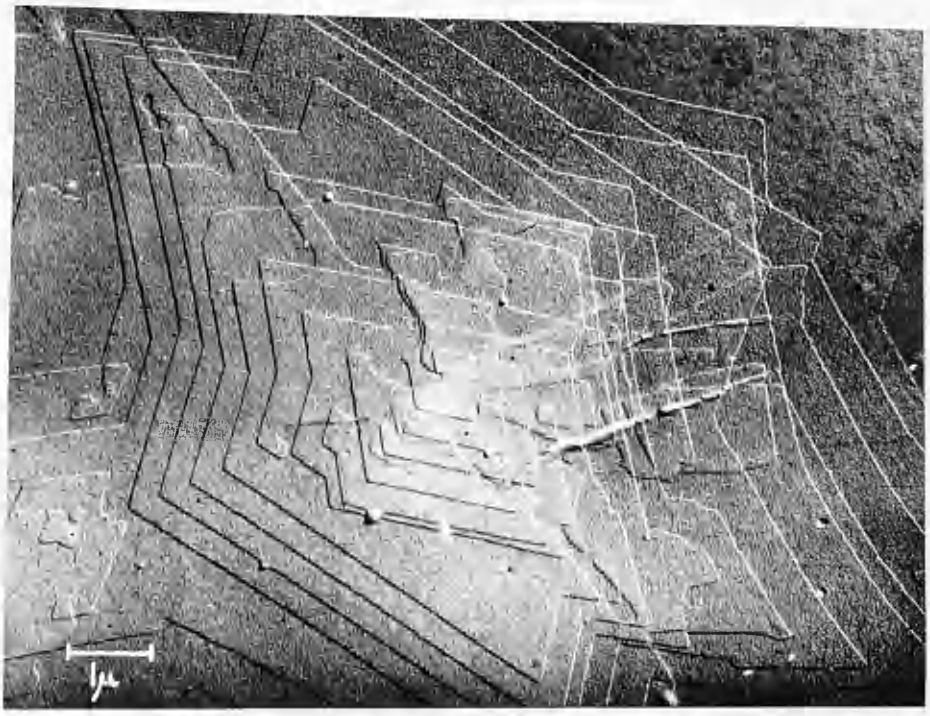


Figure 22. Electron micrograph of a crystal of a paraffin mixture. The crystal appears to consist of two intertwined crystal lattices. The multiple dislocation centre is also noteworthy

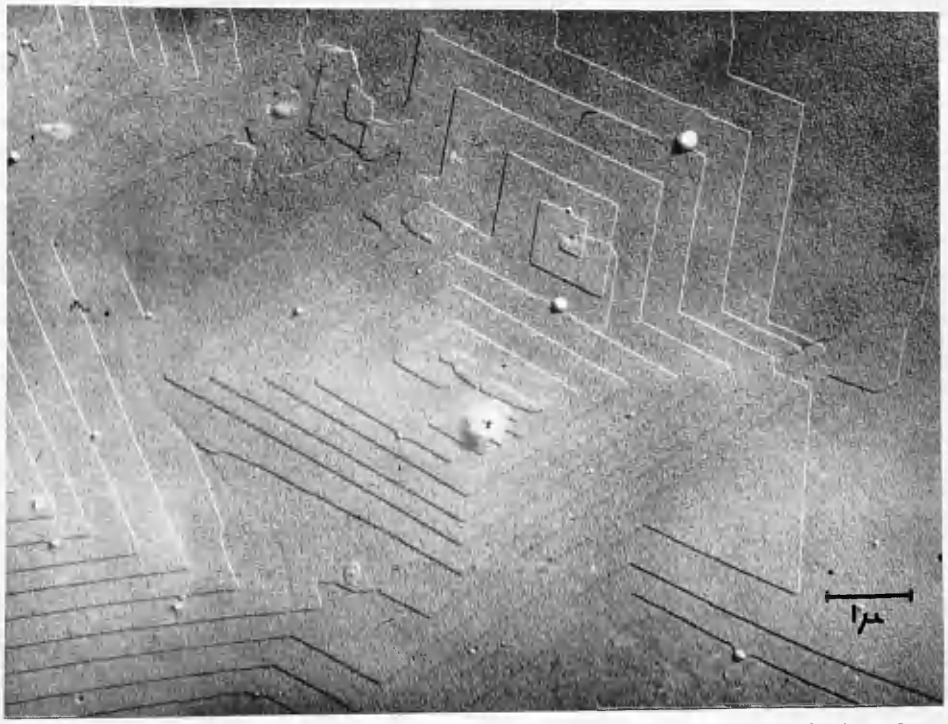


Figure 23. Electron micrograph of part of a crystal sheet in a paraffin mixture specimen. The changes in lattice orientation should be noted.

iii) Twinning.

In contrast to the specimens of the pure paraffins $C_{36}H_{74}$ and $C_{39}H_{80}$ examples of crystals twinned across the cell diagonal were encountered fairly frequently. This type of twinning gives rise to lath-like growths similar to the one shown in figure 24. Such crystals have previously been observed by Dawson (1952) in n-hectane specimens and by Dawson and Duncan (1952 unpublished)in n-dooctacontane specimens, but no examples of twinning have so far been encountered in specimens of the lower paraffins.

iv) Change of Lattice Orientation in Paraffin Sheets.

Another interesting feature observed in paraffin mixture specimens was the frequency with which the lattice orientation of crystal sheets underwent changes in direction. This is well illustrated by figure 23 where several orientations can be seen in the basal sheet. In this connection the crystal shown in figure 24 is of particular interest. The crystal in this micrograph would appear to consist of two intertwined crystals of different lattice orientation.

A related phenomenon is that the occurence of twist

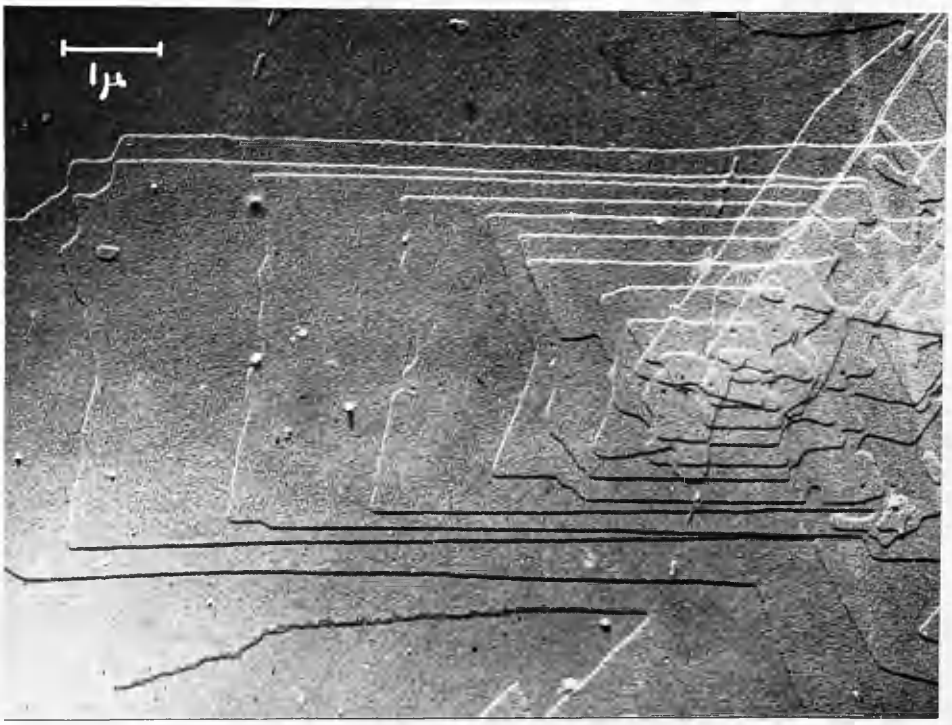


Figure 24. Electron micrograph of a twinned lath in a paraffin mixture specimen.

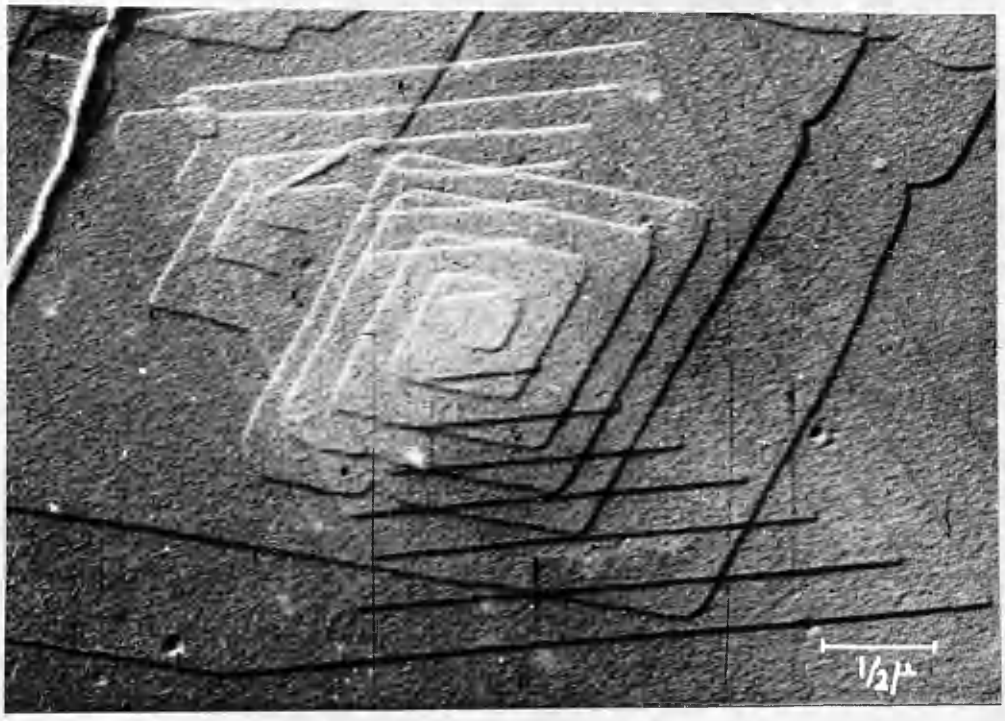


Figure 25. Part of a crystal sheet in a paraffin mixture specimen showing 'twist' from the twin position between the layers on the upper and lower faces of the sheet.

boundaries. When a crystal has spirals developed on both upper and lower faces the lattice orientation is sometimes found to be different in the upper and lower halves of the crystals. In such cases a twist boundary is said to exist between the two parts of the crystal. Since this phenomenon has been widely encountered in npropyl n-pentacontanoate it will be dealt with more fully in that part of the experimental results. It is, however, noteworthy that three examples including one of twist from the twinned position which is reproduced in figure 25, have been observed in the paraffin mixtures.

v) Polymorphism in Paraffin Mixtures.

Electron diffraction studies on the paraffin mixtures containg 53% $C_{36}H_{74}$ and 47% $C_{39}H_{80}$, and 85% $C_{36}H_{74}$ and 15% $C_{39}H_{80}$ showed that the crystals like those of the pure paraffins were generally of the orthorhombic modification. However, among the electron micrographs two crystals were encountered which had interfacial angles differing markedly from that of the orthorhombic form (67.4°). In one case the angle was as high as 74.2° and in the other it was considerably below the orthorhombic angle and was equal to 61.4°.

c) STEARIC ACID.

i) Growth Patterns.

Many of the crystal replicas examined exhibited spiral growth patterns, and among these were examples of patterns due to simple single spirals, to two or more spirals of the same sense and to the interaction of two dislocations of opposite sense. As in the case of the paraffins the arms of the spirals were generally of rectilinear form. Of particular interest were the comparatively large number of crystals with multiple dislocation centres consisting of several spirals of the same sense. Examples of such patterns are provided by figures 29 and 30. Amongst the crystals grown from petroleum ether were a fairly large proportion with completely flat surfaces. These crystals gave no evidence of growth steps or dislocations on their surfaces.

ii) Step Heights.

Difficulties were encountered in obtaining suffieiently clear-cut replicas to permit accurate measurements of step heights. However, a series of accurate measurements on ten crystals grown from petroleum ether gave a value of 47 ± 10Å which is very close to Müller's (1927) value for the length of the c-axis. One example has also been

encountered where the measurement was 27.5 ± 5Å, i.e. about half the length of the c-axis. It would thus appear that the growth steps on crystals grown from petroleum ether are generally bimolecular and occasionally unimolecular. Accurate measurements on specimens grown from benzene were not possible owing to certain features of the replicas which made the accuracy of measurements uncertain. These features will be discussed later. Crude measurements on a few crystals indicated that the steps were mainly of bimolecular heights. From this it would appear that growth of stearic acid from non-polar solvents involves mainly bimolecular growth steps.

No conclusive evidence of multimolecular steps was obtained, and, in cases where growth appeared to be based on a dislocation of multimolecular strength, considerable separation into bimolecular steps was observed. In figure 28, for example, which shows a micrograph of a crystal grown from petroleum ether, growth would appear to be based on a dislocation of tetramolecular Burgers vector. In following the growth spiral from the tip to the edge of the crystal it can be seen that the growth steps are not recognisable as separate for the first five hundred ångströms of their travel, and as growth proceeds from the growth tip towards the edge, the two spirals begin to separate. The separation distance gradually

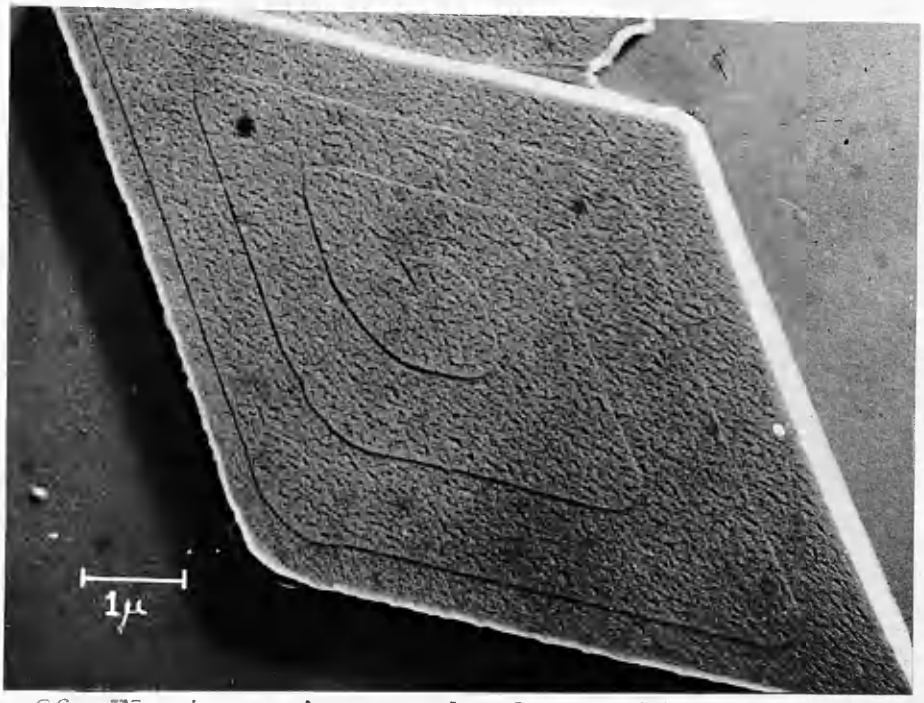


Figure 26. Electron micrograph of a replica of a stearic acid crystal of the C-modification showing growth from a single dislocation. (Grown from petroleum ether)

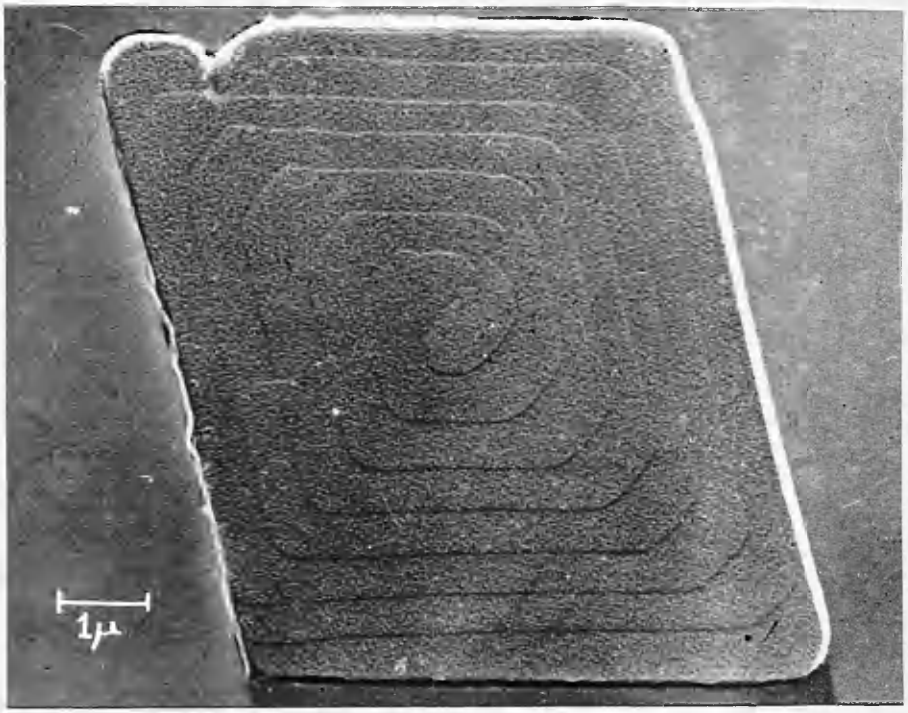


Figure 27. Electron micrograph of a replica of a stearic acid crystal of the B-modification showing a single spiral growth front. (Grown from petroleum ether)

increases until the growth steps are equally spaced near the crystal edge. Figure 31 shows an example of a crystal grown from benzene and although accurate measurements of step height were not possible in this case, it seems probable from their visibility that the composite steps are of quadrimolecular height while those into which they dissociate are of bimolecular height. It will be noted that there is a considerable tendency for the composite steps to dissociate and the spiral arms are by no means of the same height along their entire length. Consequently, it seems likely that, when dislocations with vectors of multimolecular length occur, the steps originating from them tend to undergo dissociation into bimolecular steps.

Figure 27 which shows a crystal grown from petroleum ether, exhibits an interesting peculiarity. The growth steps, although bimolecular, are out of register along a line joining the growth tip to the top right-hand corner of the crystal. There is some suggestion of half-steps connecting each turn of the spiral along this line as shown in figure 51f.

In large crystals secondary bunching of the growth steps is frequently observed as is illustrated by figure 29. This effect, although leading to local multimolecular growth steps should not be confused with the case where

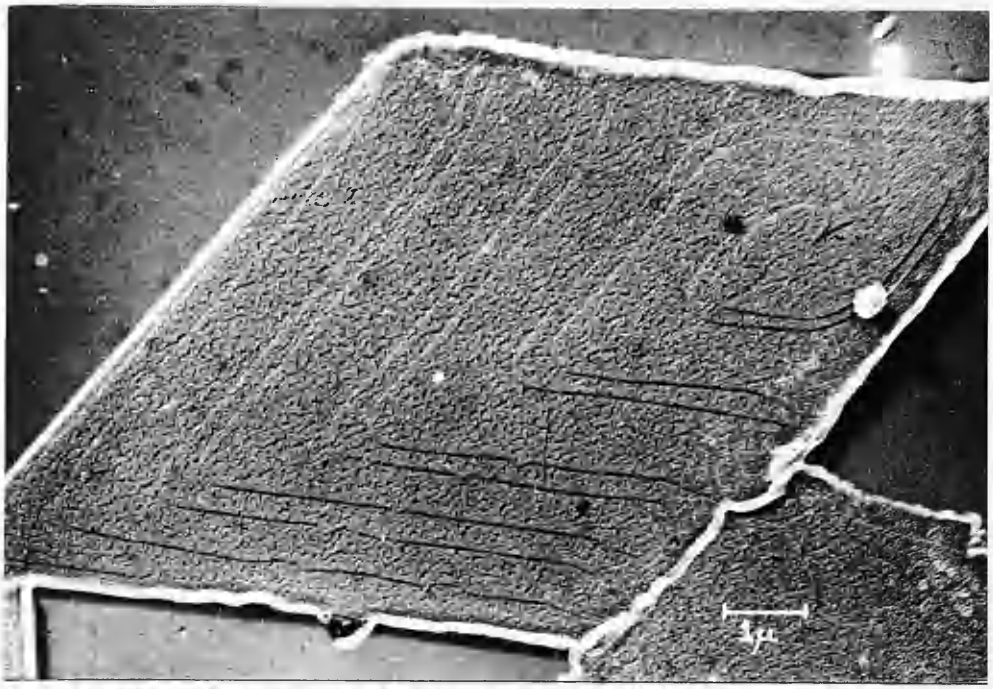


Figure 28. Electron micrograph of a replica of a stearic acid crystal Showing a dislocation with a quadrimolecular Burgers vector. (Grown from petroleum ether)

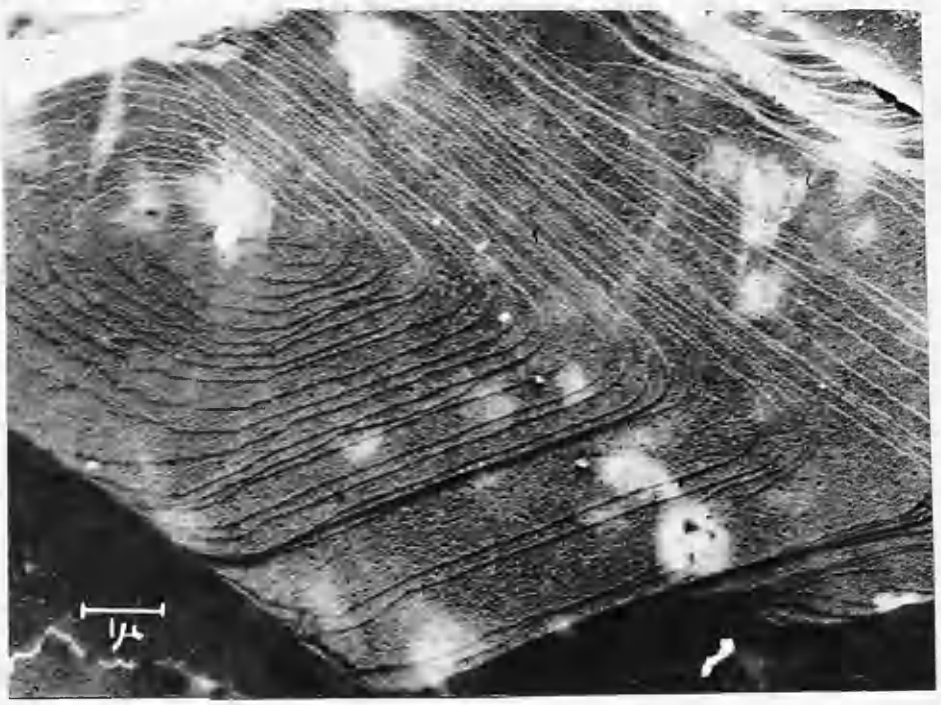


Figure 29. Electron micrograph of a stearic acid crystal (SiO replica) crystallised from benzene.

multimolecular steps arise from the presence of a dislocation of multimolecular strength. In the latter case, if no step dissociation occurs, the growth steps will be multimolecular along their entire length. In cases of secondary bunching, however, which is presumably to be attributed to local accidental hold-ups in growth, the steps are only multimolecular for very limited fractions of the total length of the spiral. Furthermore the height of such bunched steps is in no way related to the strength of the parent dislocation. Secondary bunching has previously been observed by Dawson and Vand(1951) on large crystals of n-hexatriacontane.

iii) Variations in Growth Step Appearance.

In the crystals grown from benzene solution not all the steps were identical in appearance. While some steps showed a fair degree of straightness, others were extremely uneven and ragged in appearance. This is particularly noticeable in figures 29,30 and 31. Two adjacent sets of steps were generally observed to exhibit this uneveness and both sets were situated on the same side of the crystal with respect to the b-axis (bisectrix of the obtuse angle of the rhomb in crystals of the C-modification). A similar observation has been made by Verma and Reynolds (1953) in their light-microscope study of the acid.

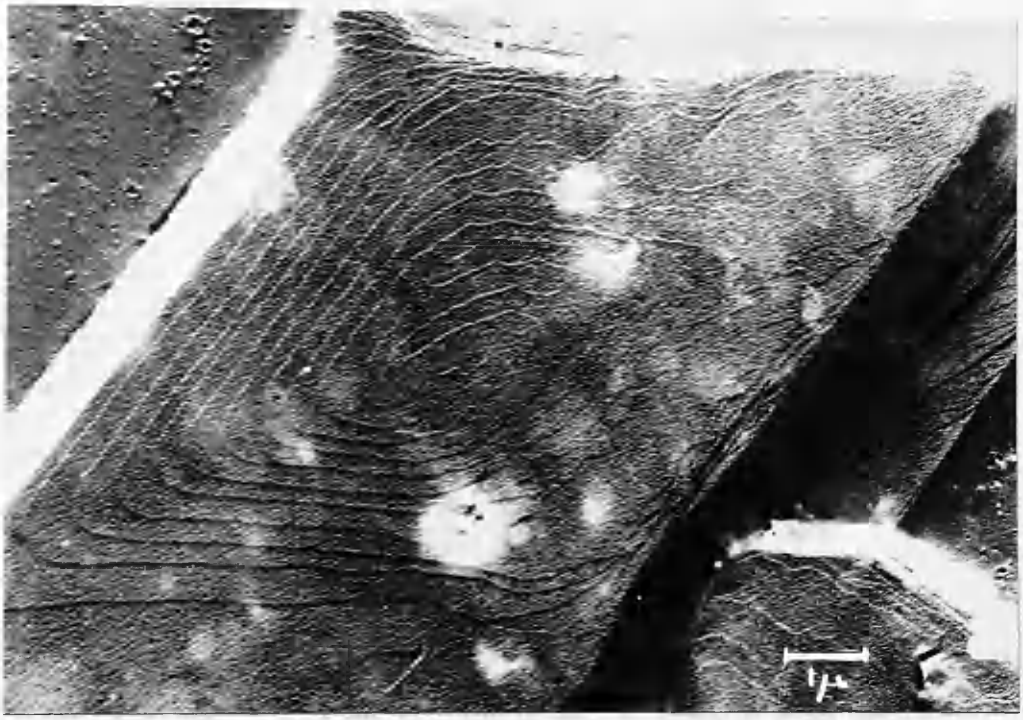


Figure 30. Electron micrograph of a replica of a stearic acid crystal grown from benzene.

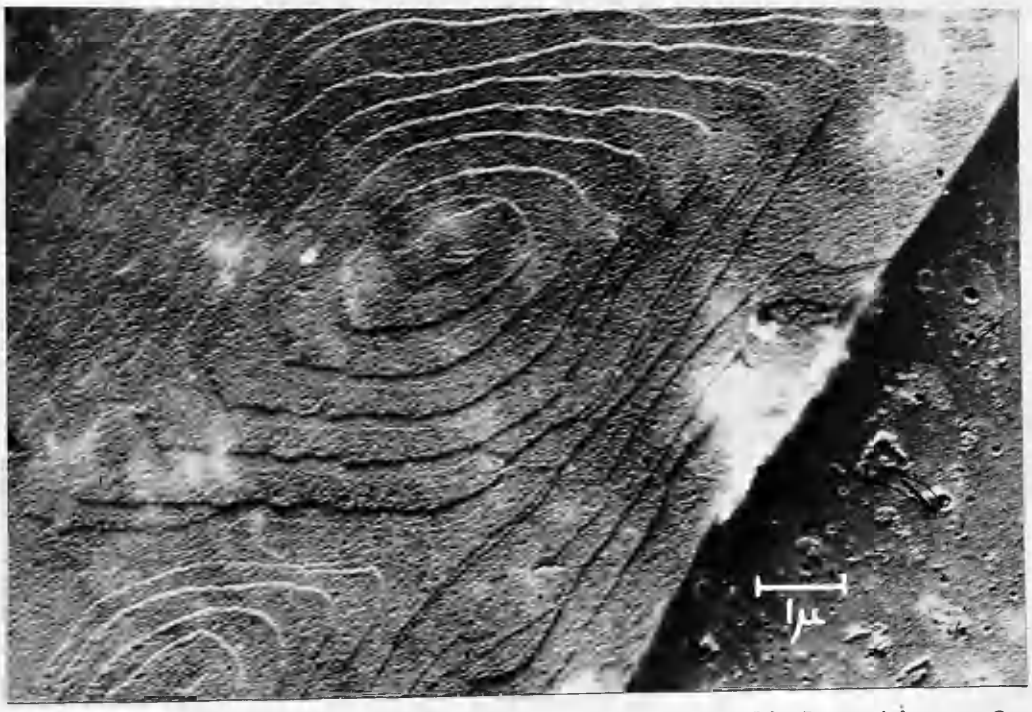


Figure 31. Electron micrograph showing a dislocation of quadrimolecular vector in a stearic acid crystal grown from benzene.

Close examination of micrographs showing this feature reveals the presence of a faint line preceeding the ragged steps.

A few specimens of crystals grown from petroleum ether were prepared in the same way as the benzene crystals (see section 111B). As will be apparent from figure 32 which is a replica of one of these specimens, the crystals exhibited a feature extremely similar to that shown by specimens grown from benzene. Again there are two adjacent sets of uneven growth steps and these sets lie on the same side of the crystal with respect to the b-axis (in this case the bisectrix of the acute angle of the crystal since it belongs to the C-modification).

It was this feature of the replicas of crystals grown from benzene that was mainly responsible for the difficulty in measuring step heights. In the first place, the step lines appear to be very diffuse, which may be due, as will be seen later, to the accumulation of crystal debris in front of them. Secondly, the white line which can be seen in front of them is nearly comparable in intensity to the white lines due to the steps on the side of the crystal facing the oncoming shadowing metal. This suggests that there may be a depression in front of the steps. In view of this any step height measurements

Figure 32. Electron micrograph of a stearic acid crystal grown from petroleum ether. This crystal was prepared by the same proceedure as those in figures 29, 30 and 31 and shows a similar etching effect at the edges of some of the growth steps.

are of doubtful significance.

iv) The Polymorphism of Stearic Acid.

Two forms of stearic acid were encountered, the B-form illustrated in figure 27 and the C form illustrated in figures 26 and 28. Both these forms are monoclinic modifications and from the electron diffraction studies the following cell dimensions were obtained: a=5.64 ±0.02Å and b=7.59 ± 0.06Å, and a=9.11 ±0.04Å and b=4.82 ±0.04Å, respectively. The specimens generally contained a mixture of the two forms, especially when petroleum ether was used as a solvent. No correlation between the conditions of crystallisation and the relative proportions of the two forms was evident from the experiments. Successive crystallisations under apparently identical conditions yield mixtures containing 23%C and 77%B, and 70%C and 30%B, respectively.

d) HEXADECANE 1,16 -DICARBOXYLIC ACID.

i) Growth Steps.

The growth steps on crystals of hexadecane 1,16 - dicarboxylic acid were extremely fine. Indeed, extremely sharply focussed pictures were necessary to reveal the presence of steps at all. Due to this fineness accurate measurements of step height were out of the question.

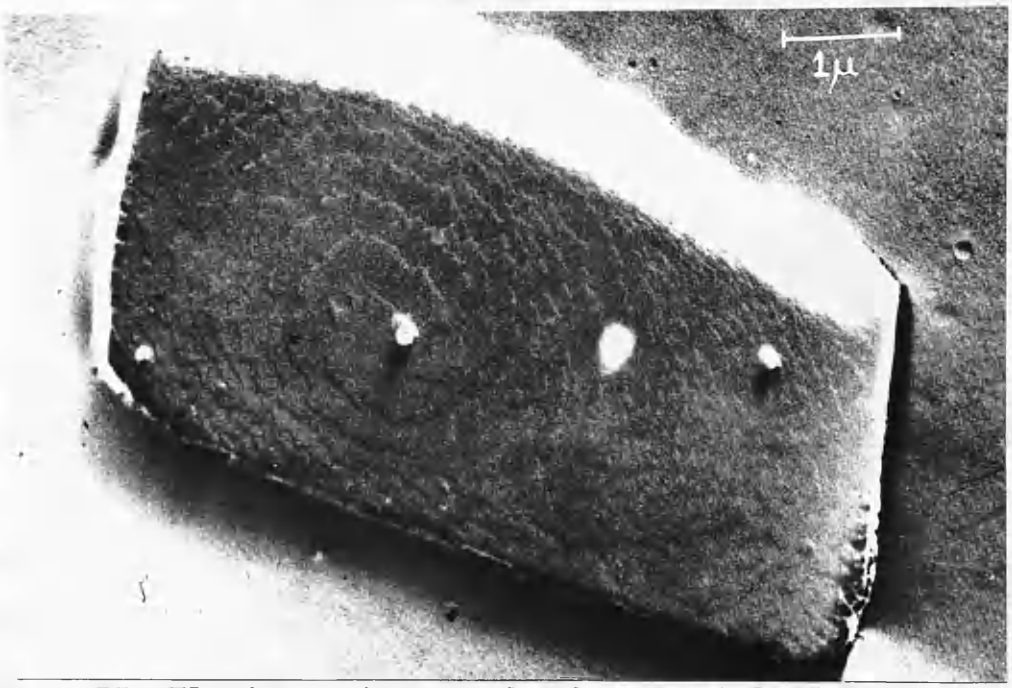


Figure 33. Electron micrograph of a crystal of hexadecane 1,16-dicarboxylic acid showing three concentric growth spirals. SiO replica.

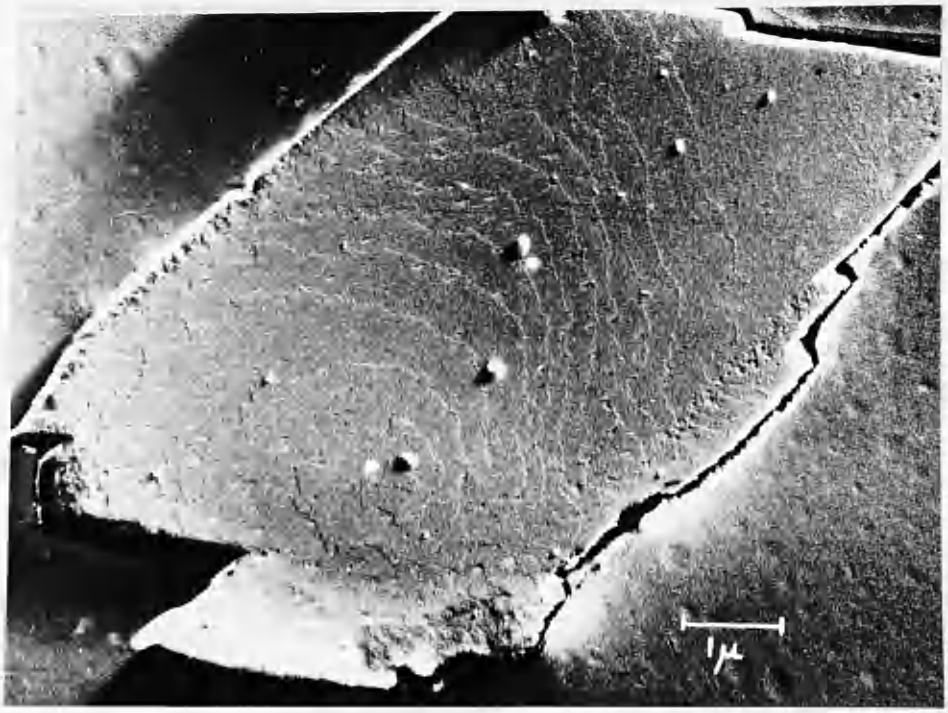


Figure 34. Electron micrograph of a crystal of hexadecane 1,16-dicarboxylic acid showing a single growth spiral. SiO replica.

However, the fact that the steps themselves are only just within the resolution of the electron microscope is in itself evidence that they are of unimolecular height.

ii) Growth Patterns.

In view of the fineness of the growth steps it was generally extremely difficult to discern the growth patterns. However, the patterns appeared in general to be of a complex nature and evidence of dislocations was seldom to be observed. The growth steps themselves showed great irregularity and uneveness and provided a complete contrast to the regular, rectilinear spirals generally observed of paraffin crystals. In addition, extreme bunching of steps was common, especially near the edges of crystals. This is well illustrated by figures 35 and 36 where very large numbers of steps can be seen near the crystal edges. A notable feature is the fact that, as will be apparent from these figures, the bunching is often confined to one side of the crystal. Sometimes extremely high steps are observed on the crystals, as, for instance, in figure 37.

In a few cases growth spirals could be discerned on the crystal faces and examples of these are shown in figures 33 and 34. The crystal in figure 33 is particularly interesting since no less than three dislocations of the

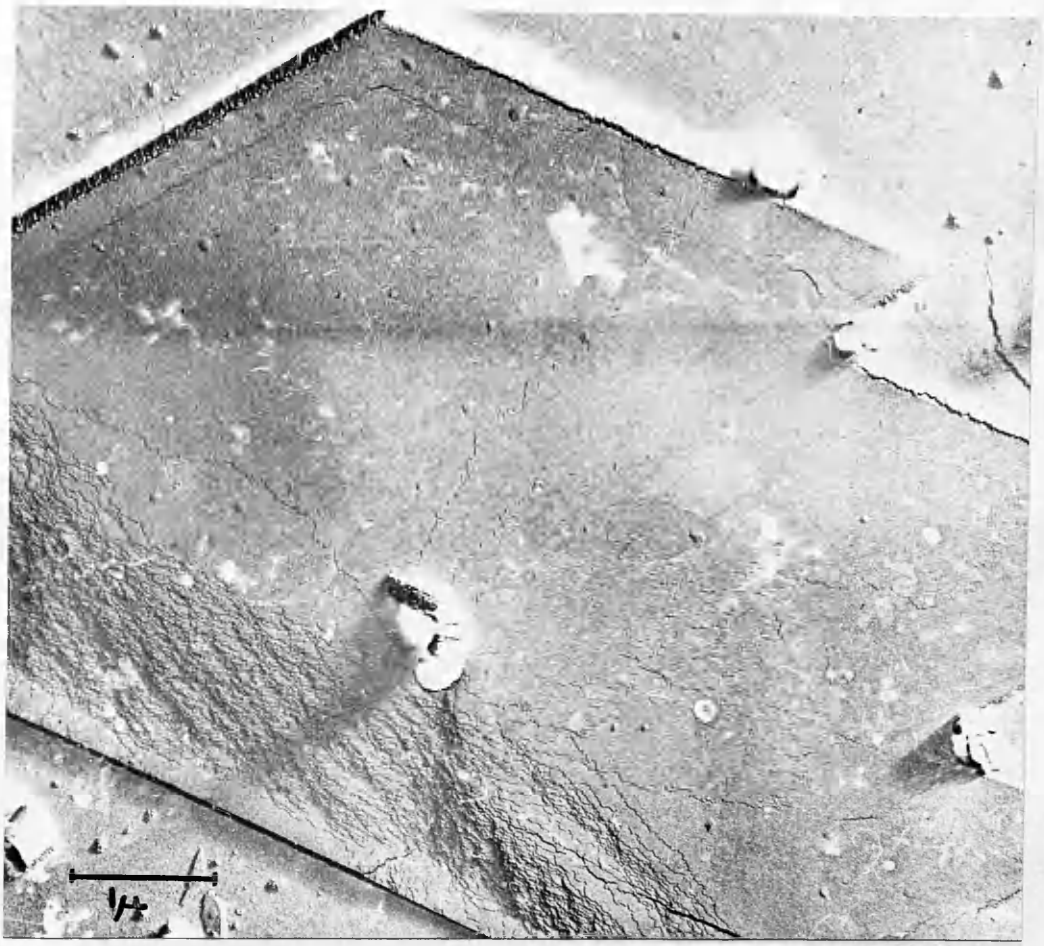


Figure 35. Electron micrograph of a formvar replica of a crystal of hexadecane 1,16-dicarboxylic acid. Considerable bunching of the growth steps can be seen near the lower edge of the crystal.

Figure 36. Electron micrograph of a formvar replica of a crystal of hexadecane 1,16-dicarboxylic. As in the previous micrograph considerable bunching of the growth steps can be seen. The steps appear to spread from left to right across the crystal.

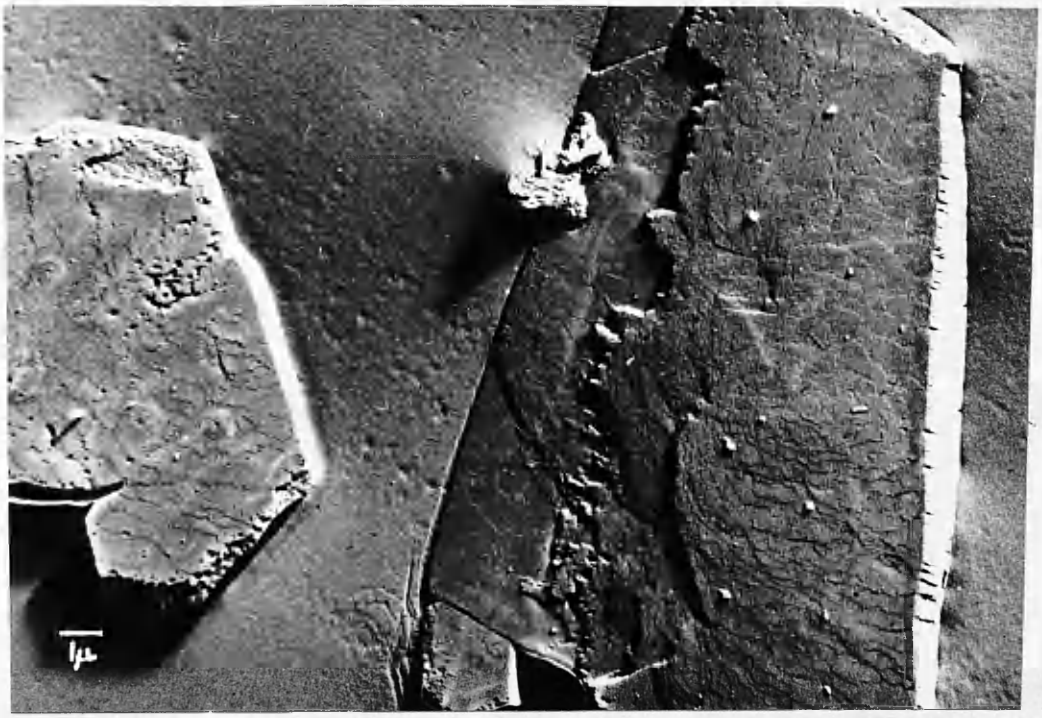


Figure 37. Electron micrograph of a SiO replica of a crystal of hexadecane 1,16-dicarboxylic acid. Besides numerous small growth steps, a step of considerable height is visible on the crystal face

same sense can be recognised. The fact that the spiral in figure 34 is well removed from the centre of the crystal is also noteworthy. In the majority of cases, however, no growth spirals were perceptible. In many crystals the steps often appeared to spread over the crystal face from edges and corners. A striking example of this is presented by figure 36 where steps appear to be proceeding from two of the edges in the bottom left-hand corner of the micrograph.

iii) The Crystal Structure of the Hexadecane 1,16-Dicarboxylic Acid Specimens.

Electron diffraction study of crystals of the acid proved difficult on account of the thickness of the specimens. The crystals themselves often lacked crystalline edges and had fragmentary appearances, as, for example, the crystals in figures 33, 34, 35 and 37. However, measurements of the interfacial angles of a few crystals where one or two crystalline edges were present, as in figure 35, gave a value $126.3 \pm 0.3^{\circ}$ which is close to the value 126.4° calculated from Caspari's (1928) measurements of the unit cell dimension. The crystals would consequently appear to belong to the monoclinic form reported by that author.

e) n-PROPYL n-PENTACONTANOATE.

i) Growth Patterns.

On examination in the electron microscope the specimens of n-propyl n-pentacontanoate were found to consist of very small crystals and a fairly large proportion of lath-like growths resembling those observed by Dawson (1952) in specimens of n-hectane. The crystals were on the whole much smaller than those generally obtained in paraffin specimens. Micrographs of the crystals revealed the presence of small steps on their faces. These steps, however, seldom formed simple spirals as in the case of the paraffins, but were often complex as is illustrated by figures 38 and 39. On closer examination of these complex patterns they are found to arise through the process of internal slip already described in the case of the paraffin n-nonatriacontane. In contrast to the paraffin crystals, however, the ester crystals appear to grow suspended in the solution so that spirals develop on both upper and lower crystal faces. On settling down on the supporting film the entire pattern on the lower face is transmitted to the upper face. The combined pattern is then rendered visible by shadowcasting.

Crystals of this type would appear at first sight to have growth patterns consisting of a succession of closed

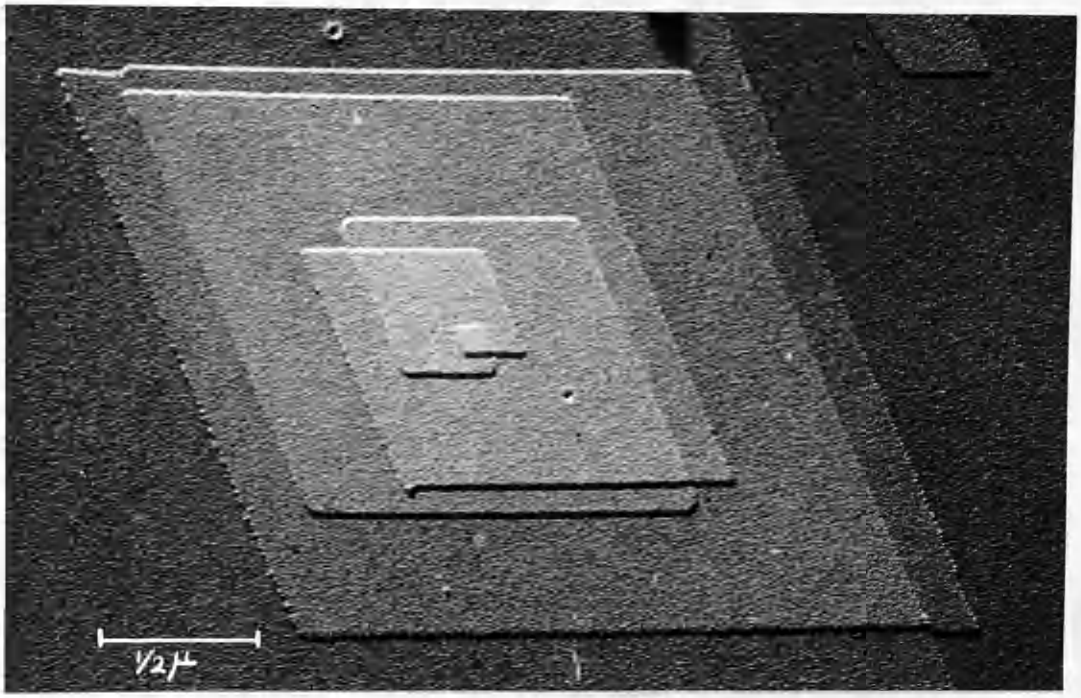


Figure 38. Electron micrograph of part of a crystal sheet in a specimen of n-propyl n-pentacontanoate. Internal slip has led to a combination of the growth patterns on the upper and lower faces

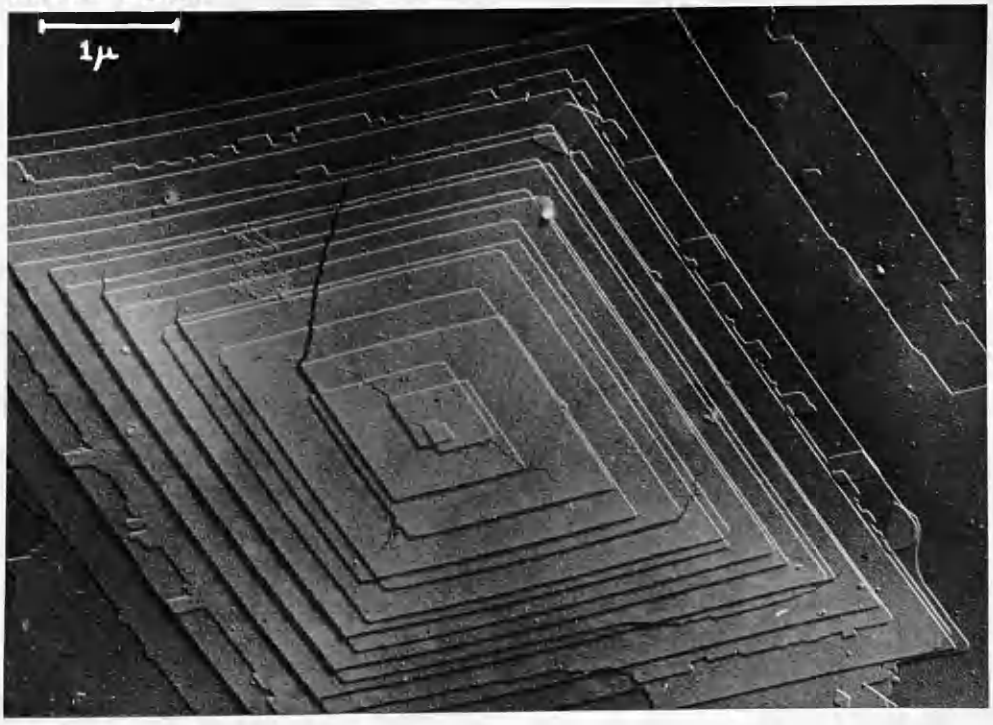


Figure 39. Electron micrograph of a crystal of n-propyl n-pentacontanoate. Cross-lacing has resulted from the combination of upper and lower growth patterns.

loops. Closer inspection, however, allows one to trace both upper and lower growth patterns. This is illustrated by the line drawing in figure 55 which shows the production of the pattern on the crystal shown in figure 38 from the original growth spirals.

ii) Step Heights.

From the lengths of the shadows cast by the steps and the known angle of shadowing the heights of the growth steps were estimated. A series of 49 crystals gave an average step height value of 81 ± 12Å. Comparing this value of 70Å found by Stallberg, Stallberg-Stenhagen and Stenhagen (1952) for the long spacing in crystals of this ester, it is clear that the growth steps are of unimolecular height.

Figure 41 illustrates a peculiarity which was observed in some cases and which tended to give an exaggerated step height value. It will be noted that the height of the lowest step of the lath shown in this micrograph appears to increase markedly towards its centre. This phenomenon is presumably to be explained either by curvature of the crystal sheet away from the substrate film or by the assumption that this film is not flat and the crystal is lying accross a depression. However, a normal step height value is obtained when measurements are

restricted to regions where this peculiarity is not in evidence.

As in the case of the n-paraffins no examples of multimolecular steps were encountered . At the same time crystals were frequently observed to have two or more dislocations of the same sense at their growth centres.

iii) Twinning.

Most of the specimens examined contained numerous examples of lath-like growth similar to those shown in figures 40 and 41. These resembled the paraffin laths observed in n-hectane (Dawson,1952) but in contrast to the latter, generally, occurred as individual growths whereas those of n-hectane frequently formed aggregates consisting of five laths radiating from a central point. In the ester specimens the laths frequently appeared to originate from a crystal which formed one end of the lath. Like the n-hectane laths those of the ester were found to be twinned accross the cell diagonal. The proportion of of laths varied considerably in different batches of specimens.

Examination of the crystals which generated the laths frequently revealed that these had spirals developed on

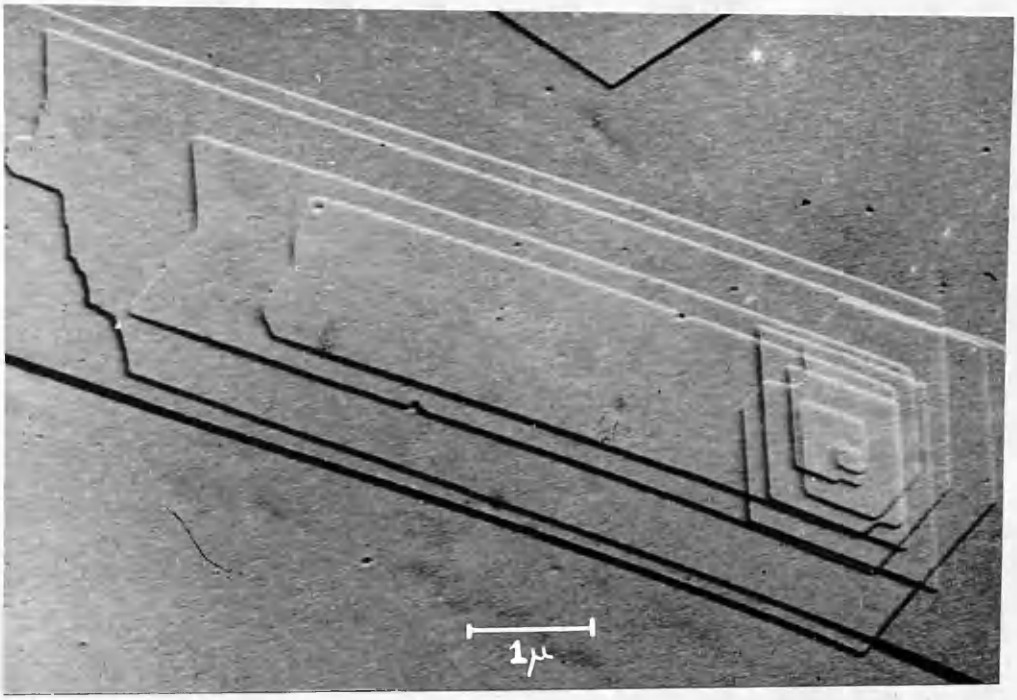


Figure 40. Electron micrograph of a twinned crystal lath of n-propyl n-pentacontaneate.

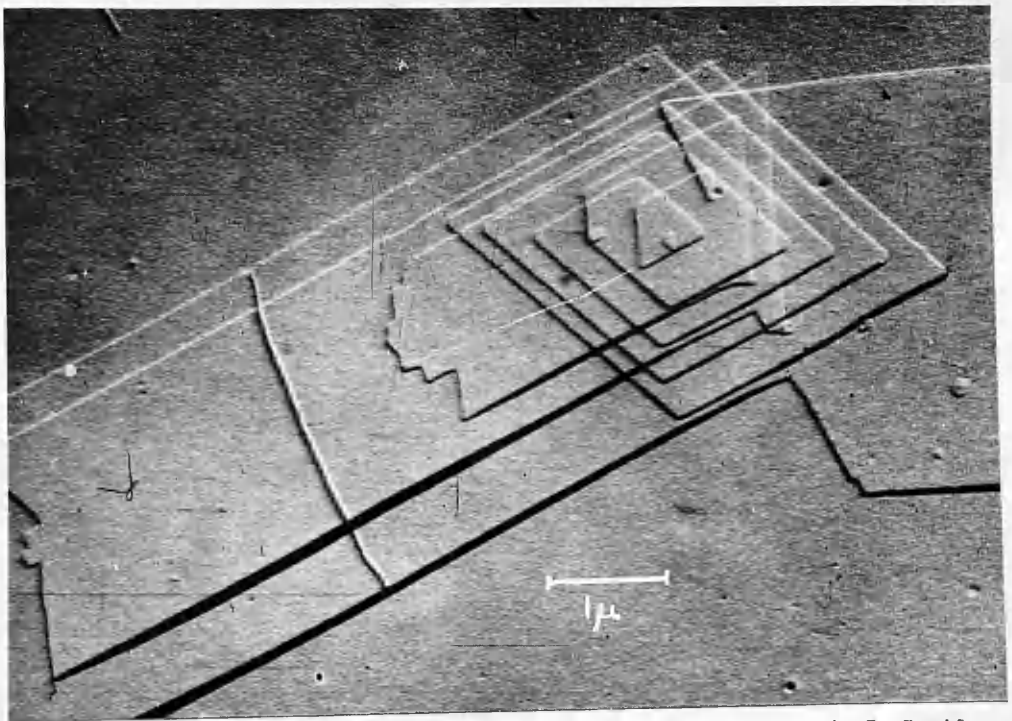


Figure 41. Electron micrographof a twinned crystal lath of n-propyl n-pentacontanoate. The apparent increase in height of the outer steps towards their centres is note worthy

both sides. The spiral on the one side was often of the normal type while that on the other, as is shown by figure 40, exhibited twinning along a line parallel to the lath direction and bisecting the crystal.

Numerous single crystals were also observed to exhibit twinning. A particularly striking example of this is shown in figure 42. At first sight this crystal would appear to have resulted from the superposition of two separate crystals. Measurement of the angle between the outermost step on the crystal face and the edge of the basal layer gives a value of 20.6° - 21.0°. This angle is close to the corresponding angle obtained when a crystal is twinned twice across the cell diagonal. The innermost steps are then obtained by a further twinning across the diagonal, so that the innermost part of the growth pyramid is related to the basal sheet by three successive twinning operations. The crystal is thus a striking example of multiple twinning.

Other single crystals were encountered where the growth pattern on the upper face was related to that on the lower by a simple diagonal twinning. An example of this is shown in figure 43. The significance of this widespread twinning will be discussed later.

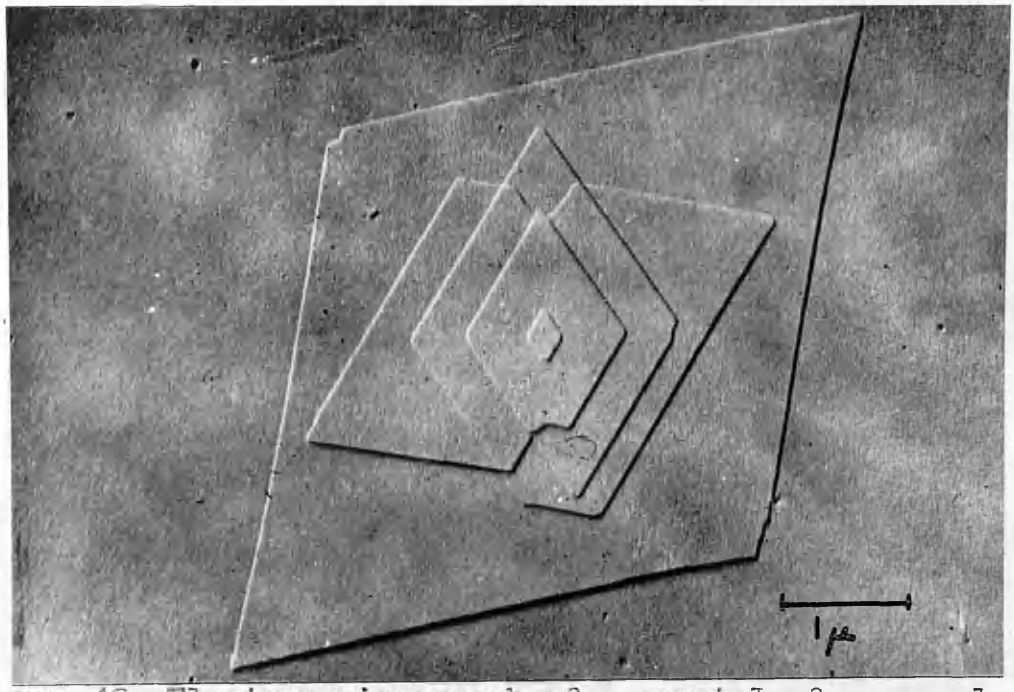


Figure 42. Electron micrograph of a crystal of n-propyl n-pentacontanoate exhibiting multiple twinning.

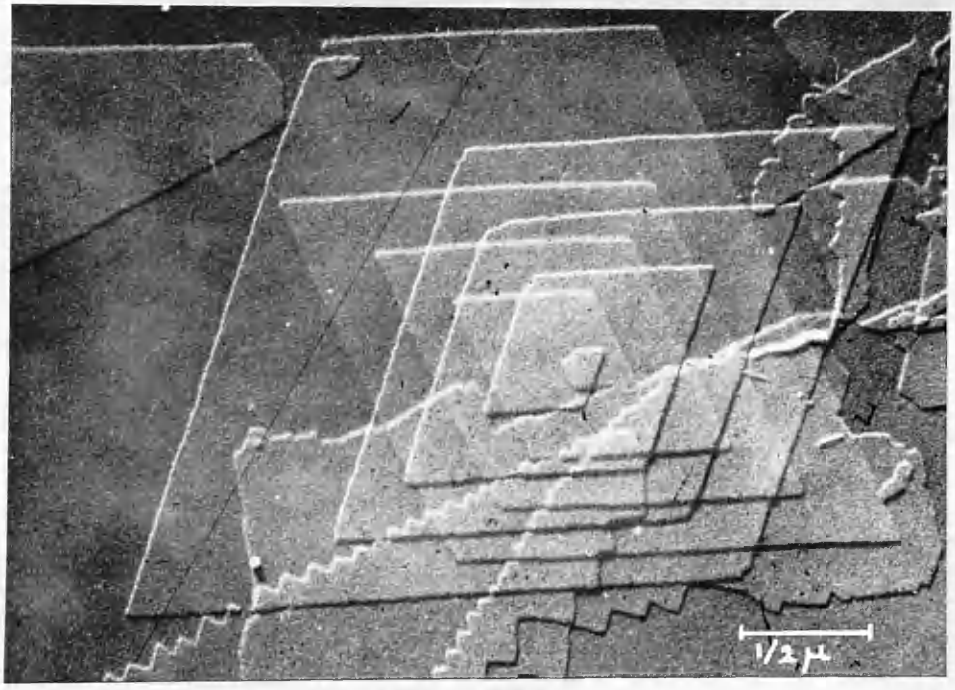


Figure 43. Electron micrograph of a crystal of n-propyl n-pentacontanoate. The lower half of the crystal is twinned with respect to the upper half.

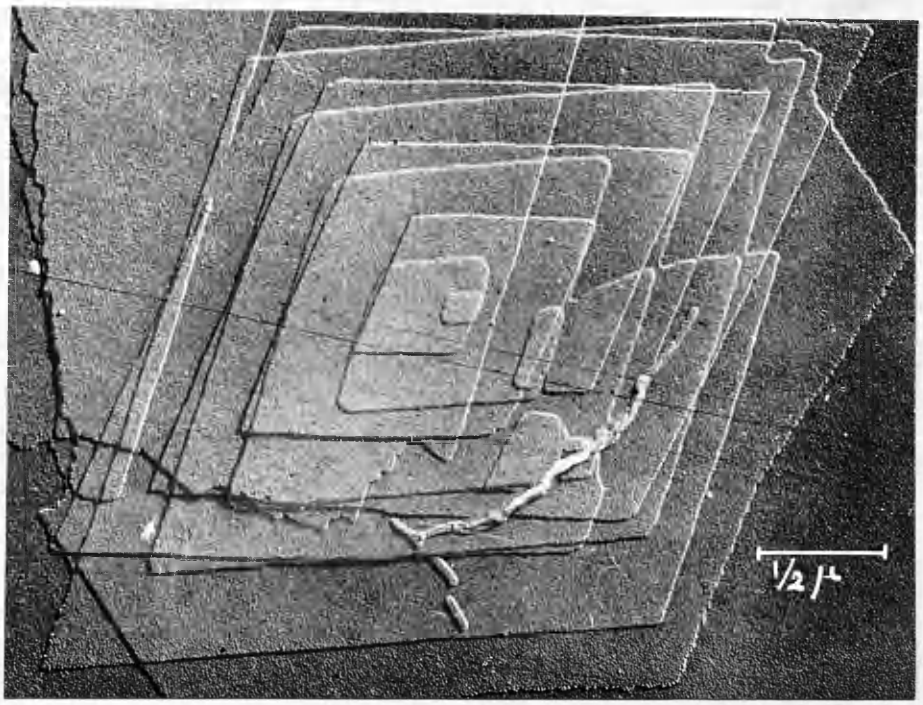


Figure 44. Electron micrograph of a crystal of n-propyl n-pentacontanoate. The presence of a twist boundary between upper and lower halves of the crystal is revealed by a difference in the directions of the steps of the upper andlower growth patterns.

iv) Twist Boundaries.

While many crystals had growth patterns which coincided completely with those which one would expect to result from the process of internal slip a small proportion showed deviations from the predicted patterns. The crystals in this group were remarkable for the fact that the steps transmitted from the lower surface were not parallel to those already present on the upper face. Typical crystals of this type are shown in figures 44 and 45. There would appear to be a twist boundary of the type described by Wilman (1951) between the upper and lower growth pyramids. The angle of twist or rotation was not constant, but, on the contrary, varied considerably as can be seen from the measurements reproduced in table II. Twist boundaries were not restricted to crystals having any particular type of growth pattern. Examples of it were observed in crystals showing patterns based on a single dislocation, two dislocations of the same sense and two dislocations of opposite sense.

As will be evident from table II., some of the values are close to the twinning angle of 67.4°. These cases in fact represent examples where the twist is better considered as rotation from the twinned position.

The proportion of crytals exhibiting twist varied

TABLE II

No.	Angle of twist	No.	Angle of twist
1	7.5°	13	8.5°
2	3.8°	14	55.9°
3	1.0°	15	8.9°
4	3.4°	16	11.3°
5	5.5°	17	7.9°,4.2° 5.0°,3.0°
6	6.4°	18	10.3°
7	3.2°	19	12.7°,9.7°
8	3.0°	20	37.0°
9	7.7°	21	27.1°
10	14.8°	22	13.0°
11	7.0°	23	12.0°
12	51.55°		

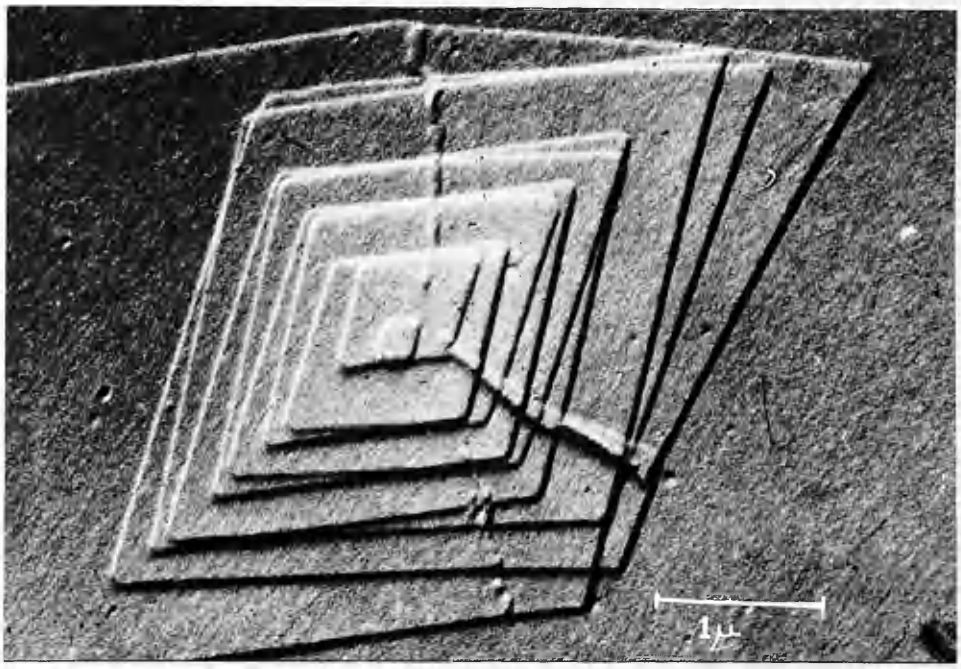


Figure 45. Electron micrograph of a crystal of n-propyl n-pentacontanoate showing a twist boundary. The twist in the outermost layer is, however, due to layer folding.

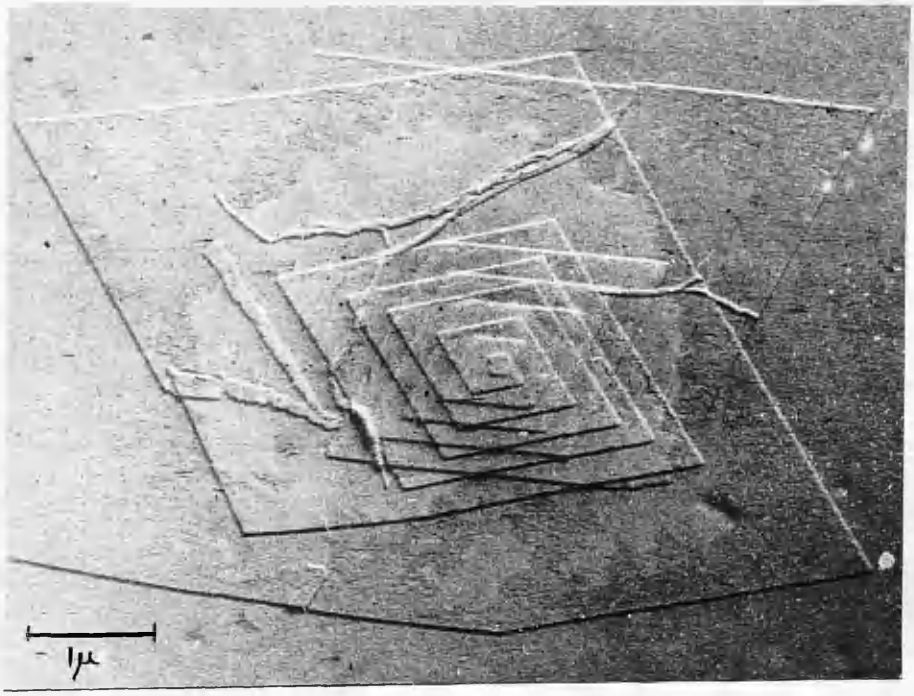


Figure 46. Electron micrograph of a crystal of n-propyl n-pentacontanoate showing a twist boundary. In this example the upper and lower halves of the crystal have undergone twist from the twinned position.

widely from experiment to experiment and did not appear to be readily controllable. In an early experiment the proportion of crystals with twist boundaries was as high as 22%, but in others it was much smaller. As it was considered possible that twist boundaries arose through rotational slip cause by stresses to which the crystal was subject to crystallization, a batch of specimens was prepared by crystallizing the ester from a hot solution in a test-tube and then placing drops of a suspension of the crystals on the specimen mounts. The additional stresses involved in this method of preparation did not appear to affect the proportion of crystals with twist boundaries to any perceptible degree.

v) Growth on the Supporting film and Nucleation.

A number of specimens were prepared by allowing drops of a hot solution to evaporate on warmed specimen mounts. One such batch of specimens was found on examination to consist of quite well developed crystals, an example of which is shown in figure 47. The growth patterns on the crystals resembled those of n-nonatriacontane grown to elevated temperatures. As will be shown later, the patterns on these crystals result from growth in contact with supporting film.

Another batch of specimens prepared under these

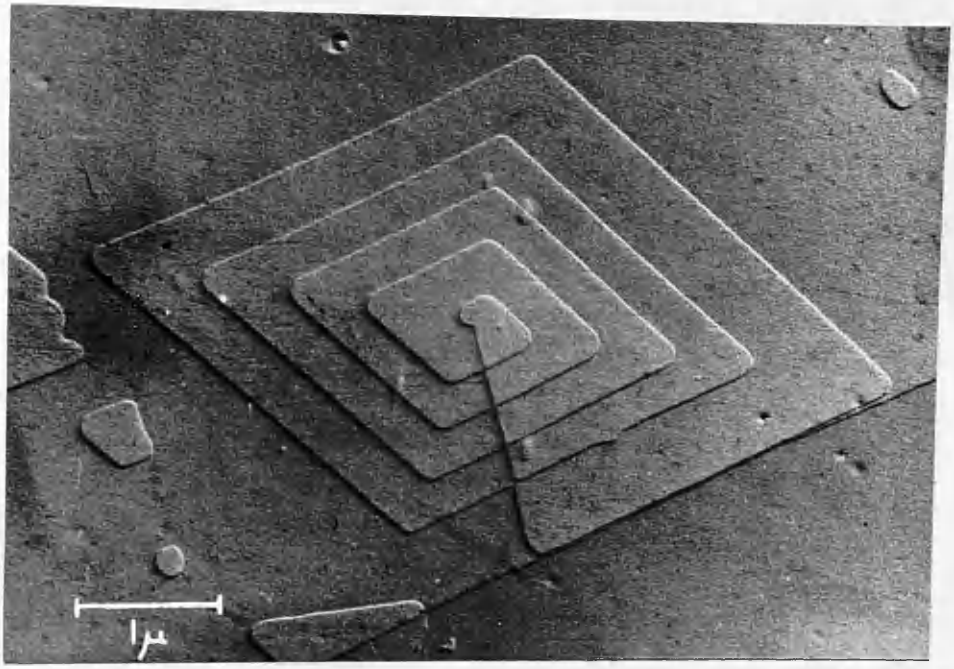


Figure 47. Electron micrograph of a crystal of n-propyl n-pentacontanoate grown from petroleum ether at an elevated temperature.

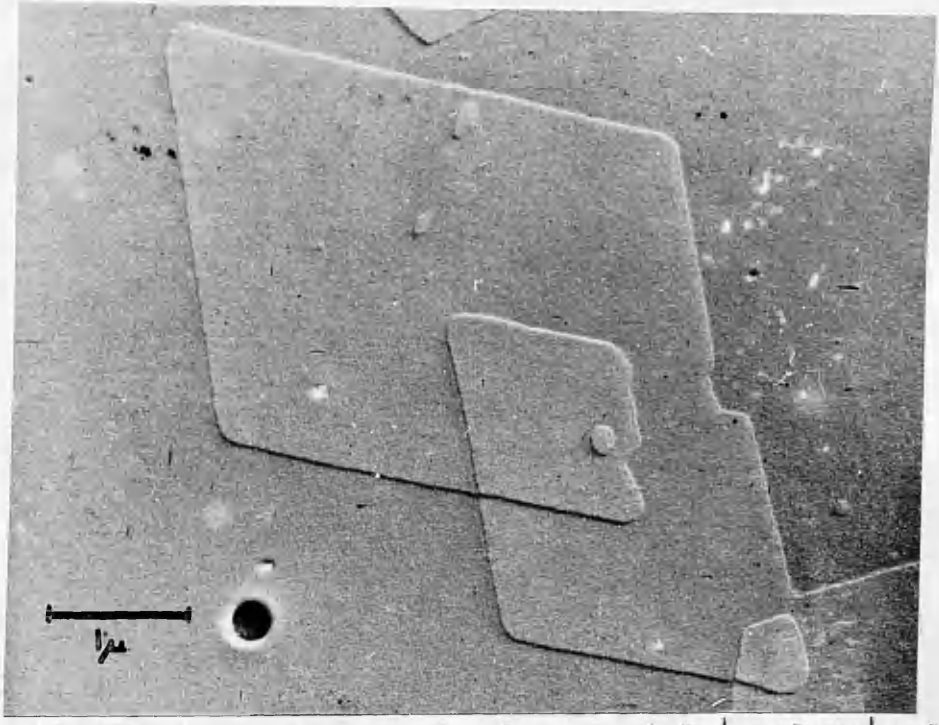


Figure 48. Electron micrograph of a crystal 'nucleus' of n-propyl n-pentacontanoate Showing an early stage in the development of a dislocation.

conditions contained few well-developed crystals but many simple crystal rhombs of unimolecular thickness, often with no evidence of the presence of dislocations and no visible surface structure. Some of these "nuclei" however possessed a re-entrant edge at one corner. Where the two segments of this edge met, an "island" was seen on the surface of the crystal. An example of this type of "nucleus" is shown in figure 48. In the crystal in this micrograph the re-entrant edges are extremely well developed. It will be appreciated that the island on the surface has arisen through the cancellation of a dislocation and these crystals, in fact, represent an early stage in the development of screw dislocations.

Another noteworthy feature of this last group of specimens is the occurrence of twinning in some of the "nuclei". Twinning is often encountered in nuclei in which dislocations have not developed.

v) The Crystalline Modification of the n-Propyl n-Pentacontanoate Specimens.

To determine the crystalline modification of the ester crystals, the specimens were investigated by electron diffraction and the following cell dimensions were obtained: $a=7.44 \pm 0.10\text{Å}$ and $b=4.84 \pm 0.15\text{Å}$. These values approximate closely to the cell dimensions of the orthorhombic

form of the long-chain paraffins and to the cell dimensions obtained by Coumoulos and Rideal (1944) for multilayers of the ester. The crystals would therefore appear to have an orthorhombic structure similar to that of the long-chain paraffins.

Measurement of the angle between $\{110\}$ and $\{\bar{1}10\}$ faces of the crystals gave a value of $67.8 \pm 0.8^{\circ}$ which agrees closely with the value 67.4 calculated for the orthorhombic form of the paraffins from Müllers (1928) values of the unit cell dimensions.

No electron diffraction patterns were obtained which could be attributed to crystals having twist boundaries present in them, and owing to the fact that electron diffraction investigations have to be carried out with low beam intensities, it was not possible to select crystals with such boundaries for individual examination.

IV C O N C L U S I O N S.

a) The Formation of Screw Dislocations.

The study of n-propyl n-pentacontanoate has thrown light on the initial stages of crystal growth in the paraffins and their derivatives. The fact that few of the small crystals grown at elevated temperatures have dislocations present in them confirms the view that dislocations do not arise during nucleation of crystals from solution but at a somewhat later stage. The nucleation stage would appear to be followed by the lateral growth of crystal sheets of unimolecular thickness. As growth of these sheets proceeds re-entrant edges arise at an edge or corner and a dislocation develops at this point. These observations present a more detailed picture than that hitherto available and differs from the hypothesis put forward by Frank (1951) in which a crystal sheet is imagined to buckle as the result of the non-uniform distribution of impurities. According to Frank's theory these strains are subsequently relieved by slip which produces a dislocation.

At temperatures above absolute zero the edge of a unimolecular sheet will not be straight, but will contain a number of kinks as shown in figure 49a. According to Burton, Cabrera and Frank (1951) the distance between kinks, x_o is given by $x_o = \frac{1}{2}a \exp\left\{\phi/kT\right\}$

where a = the intermolecular distance and ϕ = the energy of interation between nearest neighbours. For the typical case chosen by these authors in which $\phi/kT=4$, $x_0 \simeq 4a$, i.e. here is a kink for every fourth molecule in the edge. From the heat of fusion of octadecane (Oldham and Ubbelohde, 1940) which melts at 28°C, and the heat of evaporation of the same paraffin (United States National Bureau of Standards, 1949) extrapolated to 25°C it is possible to obtain an estimate of the heat of sublimation in the region of 25°C. Since this quantity, when expressed in cals./gm., will be practically independent of chain length we may use it with sufficient accuracy for the higher paraffins. By treating the crystal structure of the paraffins as hexagonal and neglecting the interaction between the chain ends, the heat of sublimation may be used to estimate the energy of interaction between neighbouring molecules. In this way ϕ/kT is found to be about 27 which gives a value of about $0.5a \times 10^6$ for x_0. This value is probably only to be treated as a qualitative indication of the distance between kinks since it properly refers to a crystal in equilibrium with its vapour. Nevertheless it shows that we may expect the distance between kinks in a unimolecular paraffin edge to be large compared with the corresponding distance in crystals of, say, iodine where the value of ϕ/kT is approximately that

used by Burton, Cabrera, and Frank.

As was first pointed out by Kossel (1927), the growth of a step will take place by the addition of molecules to kinks. In this connection the long-chain paraffins are probably exceptional in that molecules will not always add in such a way as to be in complete register with the molecules in their immediate neighbourhood. Indeed they will frequently be slightly out of register with their neighbours. Occasionally molecules will go into kinks in positions considerably out of register with the other molecules in the layer, perhaps by an amount approximating to half the length of the molecule, as is illustrated in figure 49(a). When such an event occurs, further growth along the step will probably be inhibited, unless the remaining portion BA is long enough to contain a kink. Only on the portion AC will the step continue to grow outwards. Molecules adding to this portion of the step in the region of B will probably take up intermediate positions of register, leading to a structure of the type shown in figure 49(b). In this way a partial step will be created on the upper face of the crystals which can act as a point of anchorage for condensed molecules on that face. The condensation of molecules on this partial step will subsequently lead to a structure approximating to that of a screw dislocation (figure 49c). Further growth of the

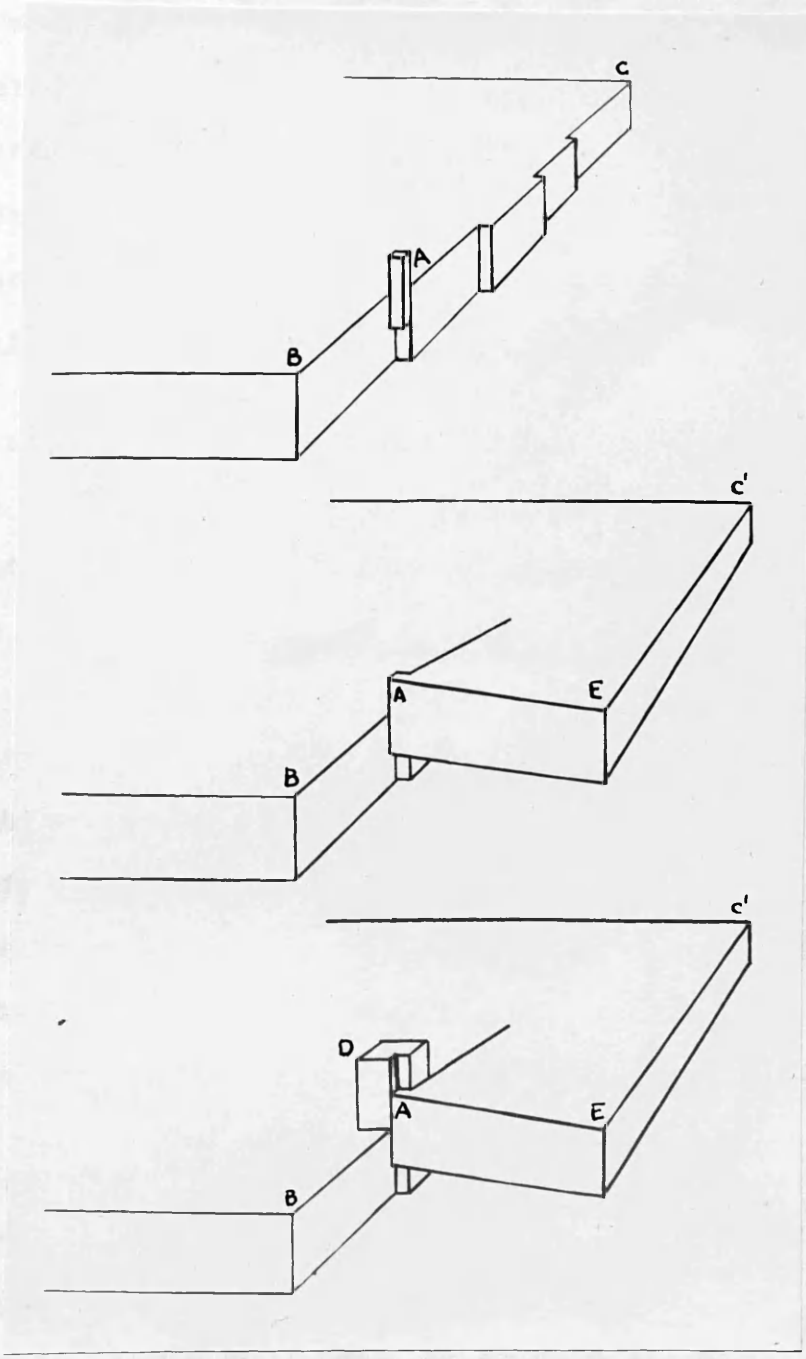


Figure 49. The formation of a screw dislocation in a paraffin sheet; (a) an edge of the sheet showing a number of kinks and a molecule added to a kink in a position of incomplete register; (b) further growth leads to configuration resembling a screw dislocation with a partial step on the crystal face; (c) adsorbed molecules adhere to the partial step on the face.

edge EC^1 will make the edge EAlong enough to contain a kink, whereafter the latter edge will proceed to grow. Fresh molecules adding to this edge in the region of A, will, under the influence of the condensed molecules attached to the partial slip on the crystal face, take up positions which will tend to make ED a continuous edge.

The assumption that the edges AB and AE cannot grow until the lengths reach a critical dimension beyond which the formation of kinks becomes possible provides an explanation of the formation of re-entrant edges in many crystals. The extent of these edges, in turn provides experimental confirmation of the prediction that the distance between kinks will be relatively large. When a screw dislocation is formed near the centre of an edge, no difference is to be expected in the development of the two actions of the crystal edge. Small differences arise, however, as the result of local variations in supersaturation.

Multiple dislocation centres arise through repetitions of the process. This is illustrated by figure 50. It will be appreciated from 50 (b) that if the crystal is resting on the supporting film the exposed edges AB and BC on the underside of the crystals may be unable to grow since they may not be of sufficient length to contain kinks. Hence when such a crystal grows resting on the supporting film the pattern on the underside of the crystal may simply

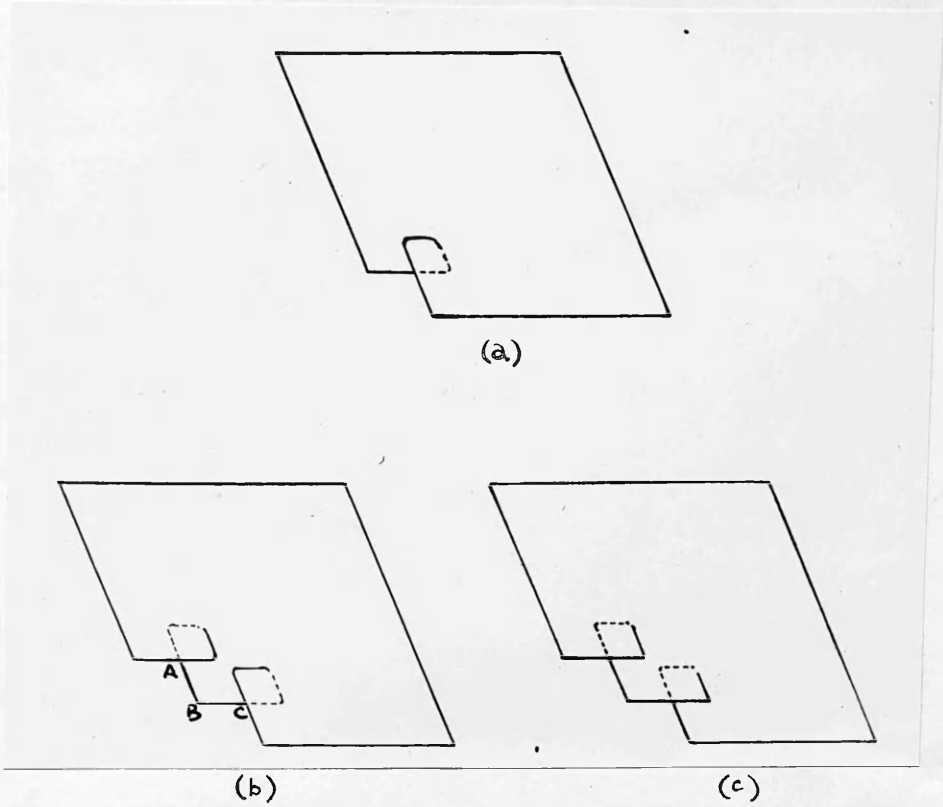


Figure 50. The formation of multiple dislocation centres.

(a) Single dislocation;

(b) Two dislocations of opposite sense;

(c) Two dislocations of the same sense.

consist of two edges such as AB and BC connecting the dislocation centres. This fact will be made use of in the consideration of crystal slip. Examples similar to those shown in figures 50 (b) and (c) are encountered fairly frequently experimentally.

The nuclei in which dislocations develop are usually extremely small. Consequently, further growth after the appearance of one or more dislocation tends to make the position of the dislocation centre approximate more and more closely to the centre of the crystal.

The theory expounded above provides no grounds for supposing that the formation of screw dislocations should be restricted to the edge of the initial unimolecular layer. On the contrary one would expect that they might also arise at step edges on crystal faces. No unequivocal evidence that this does occur has yet been obtained but it does not seem completely improbable that some dislocations do arise at step edges. For example the diagonally twinned inner portion of figure 42 may possibly have arisen in this way. It seems rather unlikely that the layers forming this part of the crystal were once on opposite sides of the basal sheet and have been united by the slip process described in section IVd of this thesis.

A crystal which provides a striking illustration of the usefulness of the theory has been observed by Dawson in n-hectane specimens. This crystal consists of a broad central sheet which is completely flat and around the edges of this sheet a series of dislocations have developed giving it a "picture frame" appearance. The specimen was prepared by allowing a drop of hot xylene to evaporate. The fact that no dislocations are formed in the initial growth of the paraffin sheet, but a large number subsequently make their appearance at the edges indicates the existence of a critical temperature, above which thermal vibrations inhibit the production of dislocations. As the sheet grows the temperature falls below this critical value and dislocations suddenly appear.

It is not surprising that dislocations should be formed by this type of mechanism in the paraffins and the derivatives. Dawson and Vand(1951) in their work on the paraffin n-hexatriacontane drew attention to the fact that the nature of the molecules guarantees the frequent occurrence of stacking faults which might in turn be responsible for the formation of dislocations. It seems unlikely at present that the same mechanism holds in the case of compounds such as cadmium iodide which have quite a different molecular structure. Indeed, it is not improbable that more than one mechanism is responsible for the formation of screw dislocations, and that the mechanism

in a particular case is determined by the nature of the molecules of the substance in question.

b) Step Heights.

The fact that the step heights in crystals of n-nonatriacontane, the paraffin mixtures, hexadecane 1,16-dicarboxylic acid and n-propyl n-pentacontanoate are of unimolecular dimensions, while those in crystals of stearic acid are generally bimolecular, confirms the view that the size of growth steps are influenced by the size of the molecular units present in the solution. This is further emphasised by the fact that steps of bimolecular height in stearic acid are not generally observed to dissociate, while steps of quadrimolecular height show a considerable degree of dissociation.

Any discussion of the influence of molecular association in solution on the heights of growth steps must necessarily start from a consideration of its effect on the thickness of the initial crystal sheet. In the case of the paraffins and esters, for example, we would expect this sheet to be of unimolecular thickness. The formation of sheets of double molecules is unlikely in these cases since it would require the nucleation by the Gibbs-Volmer mechanism of a second layer on top of the first. On the other hand, the initial crystal nucleus in the case of stearic acid is likely to be of bimolecular thickness since the solution contains mainly dimers. We may, moreover, compare the

supersaturated solution of the acid with a colloidal solution, since it contains, as well as single and double molecules, fairly large molecular aggregates ~~are~~ nuclei. There is some evidence that in colloidal solutions soap molecules, which are in essence similar to those of stearic acid, form lamellar micelles of the type suggested by McBain (1948) in which the molecules are packed in double layers with the polar groups forming the upper and lower surfaces of the micelle and the hydrocarbon chains the central portion. In a non-polar solvent this arrangement will be turned inside out so that the terminal methyl groups form the external surfaces of the micelle. Hence we may expect that supersaturated solutions of fatty acids will contain inverted micelles of the McBain type. Those micelles which reach sufficient dimensions will nucleate crystal sheets of bimolecular thickness. The possibility of the establishment of cross-linkages between individual bimolecular sheets through acid molecules in inverted positions with their carboxyl groups in the surface of the micelle cannot be excluded. It is thus possible to account for the appearance of crystal sheets of bimolecular thickness and probably also of multimolecular thickness in the nucleation of stearic acid crystals from solution.

When the initial crystal nucleus is of unimolecular thickness only dislocations of vector equal to the

molecular length can arise since the production of dislocations of multimolecular vector either by Frank's buckling mechanism or by the mechanism described in section IVa cannot be conceived. It is possible, however, to form two or more dislocations of the same sense by the repitition of the process described in the previous section (see figure 50c) and this appears to occur fairly frequently. Consequently when the compound under investigation exists as single molecules is solution, only dislocations of unimolecular strength can be formed. It should be emphasised, however, that this conclusion only applies at present to the paraffins and their derivatives.

On the other hand, when, as in the case of stearic acid the initial crystal sheet is of bimolecular thickness, dislocations of either unimolecular or bimolecular vector may arise. The growth of unimolecular steps may, however, be inhibited by the absence of single molecules in the solution. Finally, in sheets of multimolecular thickness dislocations of any vector up to that equalling the thickness of the sheet may arise. However, once such a dislocation has been formed, the growth steps originating from it will tend to dissociate into steps of height equal to the size of the growth units present in solution. This view is confirmed by the actual experimental observation of this

kind of dissociation in stearic acid crystals. The dissociation is the result of the addition of molecules to the step from the absorbed layer on the crystal face. As a consequence of this addition, more molecules reach the lowest layer in the step than reach the higher layers. The rate at which dissociation takes place, will, of course, depend on the relative importance of direct addition from the solution and addition from the adsorbed layer. Since dissociation is, as we have seen, comparatively slow in stearic acid we must conclude that the steps grow to a considerable extent by direct addition from solution.

Figure 27 is an ideal example of the usefulness of this theory of growth step height. It seems likely that this stearic acid crystal contains two dislocations, one of bimolecular and the other of unimolecular vector. The growth of the latter has, however, been inhibited by an absence of single molecules in the neighbouring solution. The bimolecular step, on the other hand has developed into a spiral but has apparently suffered delays on crossing the unimolecular step on the crystal face. This process is depicted in figure 51. In this connection it should be borne in mind that the proportion of single molecules varies with concentration and may consequently be different in solutions of different supersaturation.

The results of the electron microscope study in no way

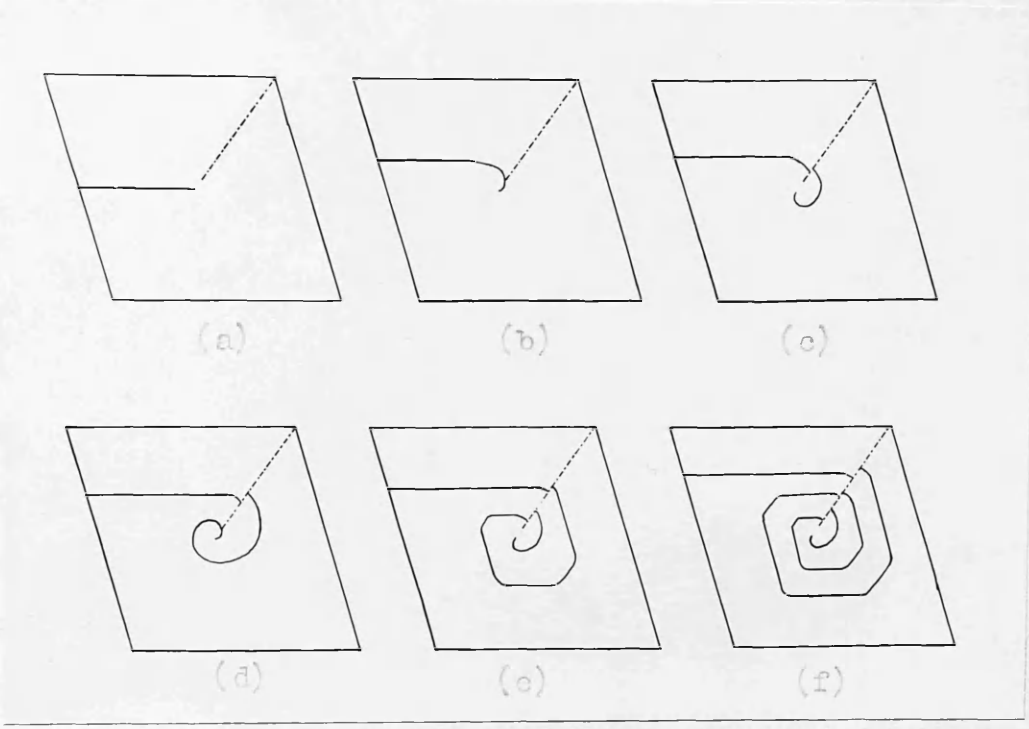


Figure 51. The growth of a stearic acid crystal from a bimolecular dislocation in the presence of an inactive unimolecular dislocation. Since no migration can take place over the unimolecular step, the bimolecular steps get out of register.

contradict the results of the light optical work of Verma and Reynolds (1953). They merely indicate that what may appear to be a single step in the light microscope may become resolved into two or more steps when subject to electron microscope investigation.

The views expressed on step height in this section may at first sight appear to be at variance with the observations on crystals of substances such as cadmium iodide. However, the extreme difference in the nature of the molecules of this compound and those of the paraffins and their derivatives must have a profound influence on the growth process. In this connection the views held by Graf (1951), for example, may be of importance in relation to cadmium iodide. The surface tension forces may make the existence of unimolecular sheets of this compound impossible. The crystal nuclei would then require to be spherical until they reached a critical dimension at which the mechanical strength of the material would balance the surface tension forces. Since cadmium iodide has a hexagonal structure, growth would thereafter take the form of the lateral growth of a multimolecular sheet in the manner suggested by Graf, and the formation of a dislocation of multimolecular vector would be possible. The resulting multimolecular growth step would, in this case, probably not dissociate since, as has been pointed out by Cabrera(1953),

the presence of slow growing layers in the growth steps of polytypic compounds such as cadmium iodide would cause the piling up of the faster growing steps.

c) THE EFFECT OF POLAR END-GROUPS.

The difference in character between the growth steps on the crystals of the paraffins and esters, on the one hand, and those on crystals of hexadecane 1,16-dicarboxylic acid, on the other, is very remarkable. While crystals of the paraffins and esters generally have rectilinear spirals made up of extremely straight steps, the growth steps on crystals of the dibasic acid, whether part of a growth spiral or not, are extremely uneven and ragged. Growth spirals when they can be discerned, are generally of circular form.

This difference in the nature of the growth patterns is almost certainly due to the difference in the chemical nature of the compounds. In the paraffins and esters the bonding between an absorbed molecule and the crystal surface is small. In dibasic acids, on the other hand, considerable attraction will exist between absorbed molecules and the crystal face on account of the tendency for hydrogen bond formation. Comparing the two cases we have in the case of the paraffins and esters.

(i) a comparatively short mean life for adsorbed

molecules on the crystal surface since they will readily re-dissolve, and

(ii) a comparatively high rate of migration since the crystal face, consisting as it does of very shallow potential energy pits, will offer little resistence to the motion of the adsorbed molecules.

In the dicarboxylic acid, on the other hand, we have

(i) a comparatively long mean life for adsorbed molecules on the crystal surface since they are much more firmly held, and

ii) a comparatively slow migration rate since the crystal surface contains deep energy pits and is therefore very rough and offers considerable resistance to the migration of molecules.

These considerations will apply equally to molecules in absorbed positions on growth steps as well as to molecules absorbed on the crystal face.

The steps on paraffin crystals are straight because they follow close-packed directions and have few kinks in them. The number of kinks in steps following close-packed directions must eventually reach an equilibrium value which has been shown by Burton, Cabrera and Frank (1951) to be determined by the energy of interaction between the molecules in the step. If the number of kinks exceeds this value

migration of molecules will take place in the edge to reduce it to the equilibrium value. If the migration rate is, however, reduced by the presence of strong binding forces of the type which exists in the dicarboxylic acids, the process of levelling out of the steps will be considerably retarded, if not effectively prevented. The occurrence of very uneven steps on hexadecane 1,16-dicarboxylic acid is completely in accordance with the above consideration of the effect of polar groups on the growth process.

These conclusions raise an important point with regard to Burton, Cabrera and Frank's (1951) derivation of the expression for the distance between kinks. Their derivation takes no account of the surface on which molecular migration takes place. This is not unnatural since they consider only the simple case of symmetrical molecules. It is now clear, however, that when the molecules are of an unsymmetrical nature, the nature of the attractive forces between adsorbed molecules and the crystal face must exort a considerable influence on the process of kink formation.

d) Internal Slip and the Movement of Dislocations.

The results obtained with crystals of n-nonatriacontane and n-propyl n-pentacontanoate suggest that screw dislocations in these crystals are only stable when the crystal is supported by a buoyant medium as is the case when growth takes place from solution. As the solvent evaporates, however, the crystal settles on the supporting film and undergoes collapse probably as a result of surface tension forces when the crystal is surrounded by a residual droplet of the solution, or the adhesive forces between the crystal and the substrate film. As the n-hexatriacontane observations indicate, this type of collapse will be favoured by high temperatures, since the greater thermal vibrations will weaken the forces between molecules.

As we have seen in the foregoing results, two types of crystal are seen to arise in n-nonatriacontane depending on the temperature at which crystallization takes place. The first type is characterized by sharp corners and the presence of well-defined growth spirals. The second which results from crystallization at elevated temperatures is notable for rounded corners and the lack of immediate evidence of growth by the dislocation mechanism. The micrographs of this latter group of crystals, which show a succession of closed loops, at first sight suggests

that growth has taken place by the classical Gibbs-Volmer growth mechanism previously described. However, if this were the case one would expect nucleation to take place at random over the crystal face whereas the growth patterns on these crystals show a striking regularity.

When a screw dislocation is formed in a crystal, in the case of the paraffins and their derivatives, by the mechanism described in section IVa, or in the other cases by Frank's buckling mechanism, a molecular step is formed on both the upper and lower faces. If the crystal grows resting on the substrate film the step on the lower face cannot develop into a spiral. A spiral growth step does, however, develop on the upper face. On evaporation of the solution from which the crystal has grown, collapse takes place along the line of the step on the lower face. This state of affairs exists in figure 14, where, as well as the spiral growth step on the upper surface, a step can be seen running from the growth tip to the edge of the crystal. This step is that produced by the transmission, of the one originally present on the lower face through the crystal to the upper face. When further growth takes place as the result of the presence of molecules which are still mobile on the face, as will be the case in the specimens grown at elevated temperatures, the corners of the steps become rounded and the type of pattern illustrated by figure 15

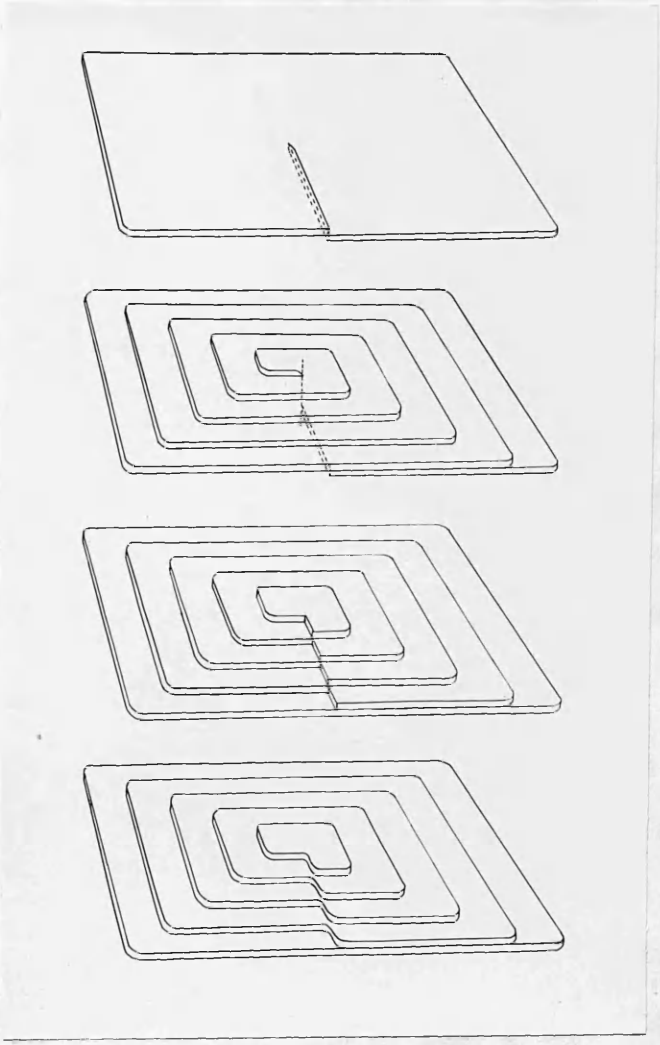


Figure 58. The effect of the cancellation of the dislocation on the appearance of a growth pyramid originally consisting of a single spiral. (a) The formation of a screw dislocation in a crystal monolayer; (b) subsequent growth on one side only, giving rise to a spiral growth step; (c) collapse of the crystal along the line of the step on the underside; (d) appearance of the growth pyramid after further growth.

results. This process involves the cancellation of the original dislocation and is illustrated in figure 52 which shows the successive stages diagramatically. For the purpose of clarity the dislocation is represented as being produced by the buckling mechanism in figure 52(a) but it should be borne in mind that in the paraffins and their derivatives, at least, the mechanism is that described in section IVa. Figure 52(b) shows the development of a spiral growth step on one side only, (c) the cancellation of the dislocation and (d) the situation after further growth.

A similar process can occur when two dislocations of opposite sign are present. As has been pointed out in IVa, the pattern on the lower face of the crystal which grows resting on the substrate film consists of two steps such as AB and BC (figure 50b) joining the dislocation centres. In passing it will be noted that this presents a contrast to the Frank theory where one might expect each dislocation to be joined to the crystal edge by a separate step. As is well-known, the presence of two dislocations of opposite sign produces a pattern consisting of a series of closed loops. The innermost step of the growth pyramid, however, forms a closed loop but terminates on the dislocation centres. The effect of transmitting the steps on the lower surface through the crystal to the

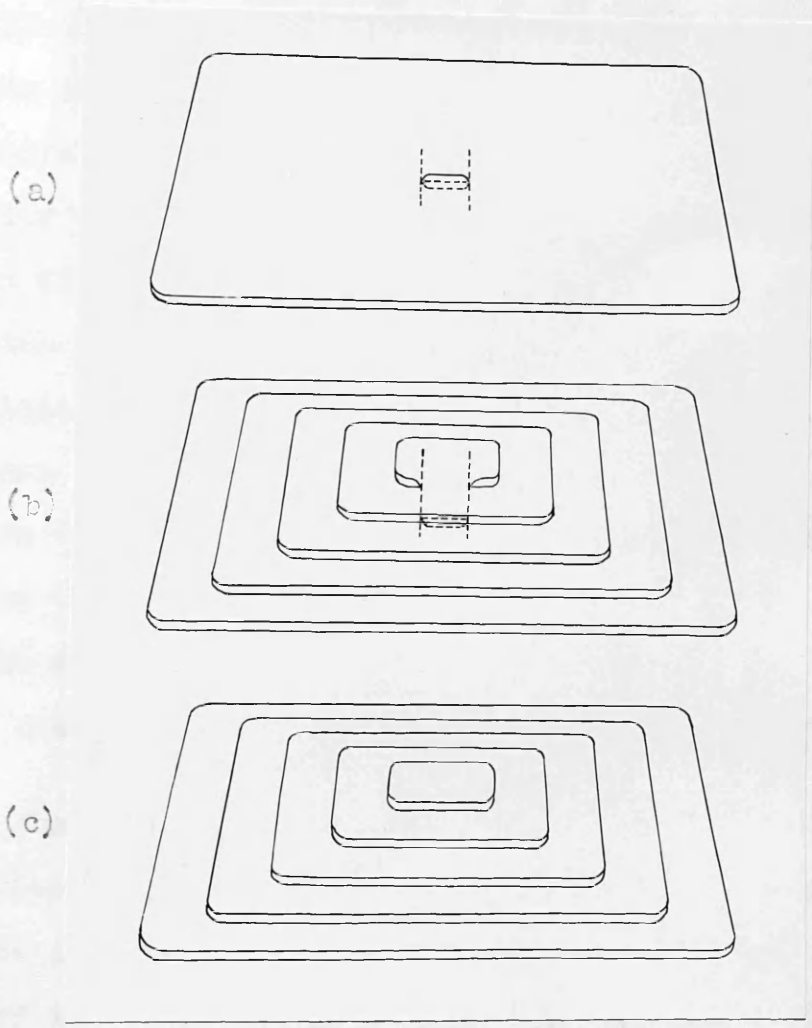
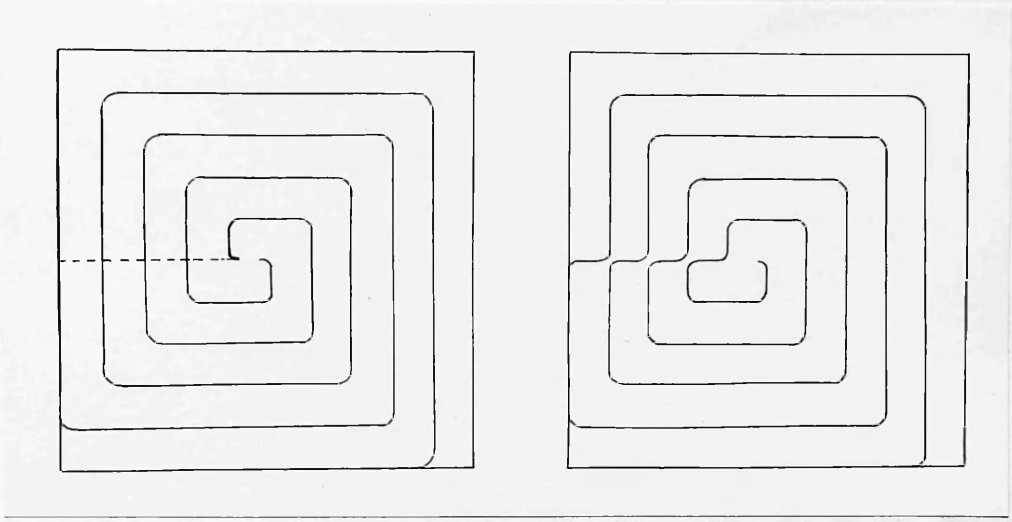


Figure 55. The effect of cancellation when two dislocations of opposite sense are involved. (a) Crystal monolayer with two dislocations of opposite sense joined by a step on either side of the monolayer; (b) growth, on one side of the layer only, gives rise to a growth pyramid consisting of closed loops with two dislocations visible in the centre; (c) collapse of the crystal along the line of the step on the underside, cancelling the two dislocations

upper face is to convert the central step into a closed loop. Figure 53 is a diagrammatic representation of the course of events in this case. In this figure the pattern on the lower surface has been represented by a single step for simplicity although in most cases it will have the form shown in figure 50(b). Figures 16 and 17 provide experimental examples of this case, the latter bearing the same relation to the former as figure 15 to figure 14. If further solvent is added during preparation, as may happen as the result of the tendency of the solution to spread on the formvar film, crystals similar to the one in figure 18 may result. This example represents and intermediate stage in the production of flat-topped crystals.

In some circumstances cancellation of dislocations would appear to take place during growth. Thus figure 20 can be interpreted as the result of the cancellation of one of the dislocations in a growth centre consisting of two dislocations of the same sign. This has produced a series of kinks in the growth steps. A diagrammatic representation of this case is given in figure 54.

In the case of n-nonatriacontane the result of the step process is identical with that produced by the movement of dislocations in crystals. Thus patterns comparable to those observed on crystals of this paraffin have been



(a) (b)

Figure 54. (a) A crystal having two dislocations of the same sense, and (b) the appearance of the growth step after one of the dislocations has been cancelled.

observed by Forty and Frank (1953, on silver crystals and have been attributed by these authors to the movement of dislocations. However, there are strong grounds for believing that the patterns observed in the present work are due to internal slip as already indicated and not to the movement of dislocations. Firstly, the slip phenomenon is observed where no dislocations are involved, as, for example, in figure 19. In the overlying crystal sheet shown in this micrograph, slip has apparently gone to completion along the lines of the steps of the underlying crystal. Secondly, the interpretation of the n-propyl n-pentacontanoate observations on the basis of dislocation movement would be difficult. In crystals of this compound the step on the lower face is not a straight step joining the dislocation centre to the boundary of the face, as in the case of n-nonatriacontane, but has wound itself into a growth spiral. On settling on the film the entire spiral pattern on this face is transmitted through the crystal to the upper face, and the observed pattern is a combination of the spiral patterns on the upper and lower faces. A diagrammatic representation of this process is given in figure 55. An interpretation of these observations on the basis of dislocation movement would require the dislocation to move along a path marked out by the growth pattern on the lower face of the crystal. Since such

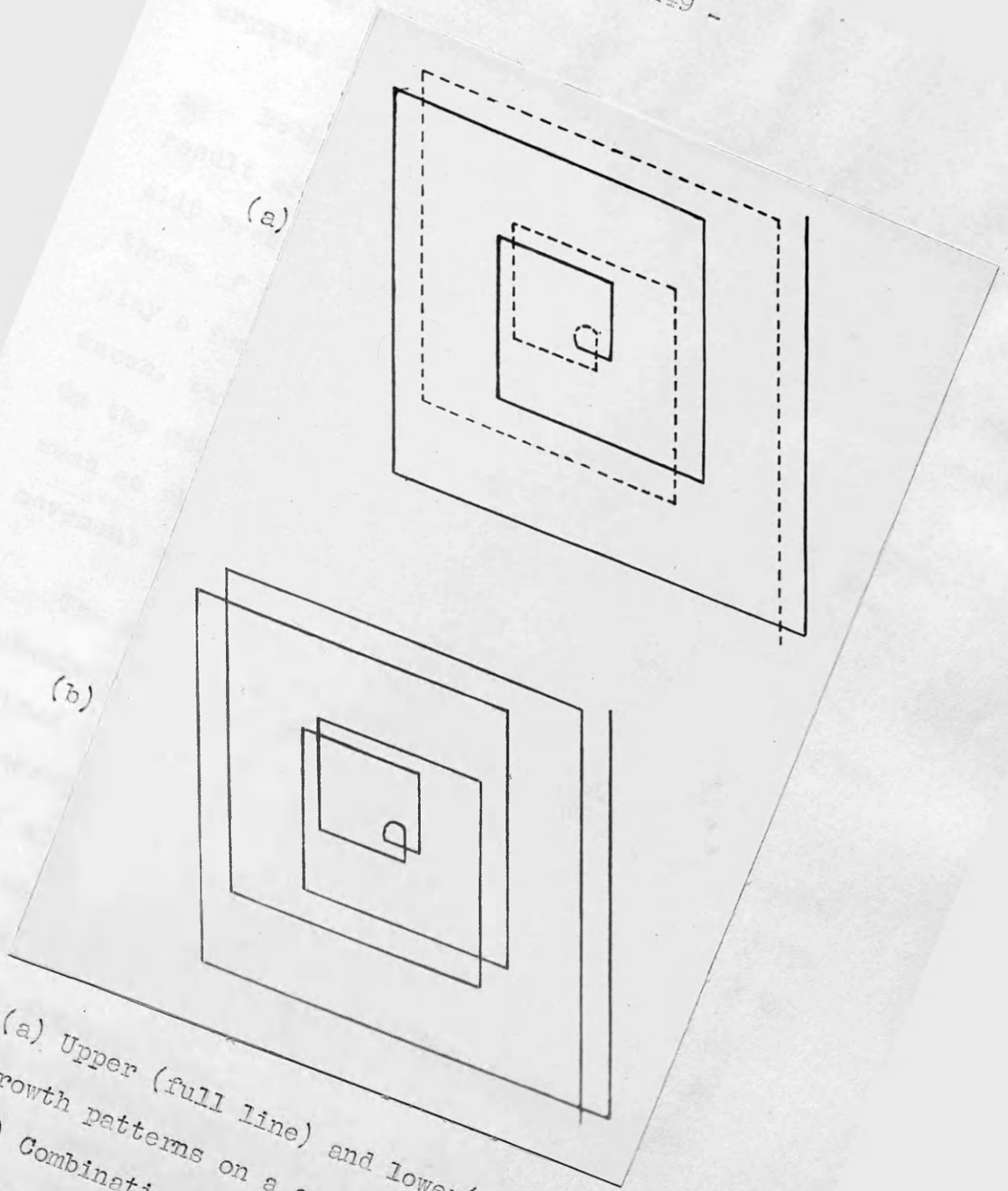


Figure 55. (a) Upper (full line) and lower(dotted line) growth patterns on a crystal.
(b) Combination of the two patterns as a result of crystal slip.

a complex mode of travel is unlikely, it follows that the patterns must be interpreted as the result of internal crystal slip.

Both slip and dislocation movement are, however, the result of the application of external stresses. Internal slip probably occurs only in very thin crystals such as those of the paraffins. Dislocation movement will not play a fundemental role in such cases, since, as is well known, the crystal sheets readily undergo deformation. On the other hand, the deformation of thicker crystals such as those of silver will almost certainly require the movement of dislocations.

The results observed in the case of n-nonatriacontane emphasize the fact that the lack of direct evidence of the presence of dislocations does not prove that dislocations have never been present. Thus dislocation movement or crystal slip may account for the fact that dislocations are not observed in some compounds and that in others the proportion of crystals with spiral growth steps on their surfaces is extremely low. In any given compound the proportion of crystals with visible spiral growth steps will depend on a number of factors including the mobility of dislocations, the ease of crystal slip, the thickness of the crystals, and the strength of the material.

Amelinckx (1953c) in a light microscope study of the long-chain paraffins and their derivatives has claimed the presence of step cross-lacing in crystals of the n-alcohols and n-fatty acids (private communication) and has attributed this to polytypism. Similar observations have been made by Verma (1954). The present work makes it seem likely that the interpretation of these observations as the result of polytypism is incorrect and is the result of the lower resolving power of the optical microscope in the object plane. Features resembling cross-lacing frequently occur in the esters when the steps of the pattern on the lower face coincide with those on the upper face. This is illustrated by figure 39 where considerable cross-lacing can be seen. It thus seems likely that the phenomena observed by Amelinckx and Verma are the result of internal slip.

e) TWIST BOUNDARIES.

The investigation of n-propyl n-pentacontanoate crystals has thrown some light on the work of Wilman(1951) who, from an investigation of a large number of diffraction patterns, showed that twist boundaries occurred in a wide variety of crystals. Wilman accounted for this observation by suggesting that, besides the position of complete register between two superposed layers of molecules, there were a number of orientations in which a sufficient number of coincidences occurred between molecules in the two layers to produce metastability. If a perfect crystal were subjected to an external stress, it might therefore undergo rotational slip between the molecular layers and come to rest in these positions of metastability.

Among the substances studied by Wilman were two paraffins n-$C_{20}H_{42}$ and n-$C_{32}H_{66}$, two alcohols, n-$C_{16}H_{33}OH$ and n-$C_{18}H_{37}OH$, and the iodide n-$C_{17}H_{35}I$. In the paraffins an angle of 61° was observed, this being slightly less than the twinning angle 67.4°. In the other cases angles about 30° and 40° together with some small angles comparable to those observed in the present work were encountered.

An examination of the twist possibilities in the paraffin type of lattice on the basis of Wilman's views, shows that the second most stable orientation of two super-

posed layers of molecules occurs when one is rotated through an angle of 68° with respect to the other. Other stable positions occur when the angle of rotation is $15^{\circ}23^{I}$, $7^{\circ}47^{I}$, $5^{\circ}9^{I}$ and a series of others corresponding to increasingly smaller angles. With these small angles, however, the number of coincidences becomes extremely small and it seems improbable that these positions will be metastable to any marked degree on account of these coincidences. Furthermore the observed angles bear little relation to those calculated, and in fact many intermediate angles are observed. The binding between successive paraffin layers is , moreover, extremely weak even compared with that within the layers (Daniels,1953) and consequently the relative orientation of two superposed paraffin or ester layers is relatively unimportant in the discussion of the problem. As the observations suggest, any orientation can occur and the cause of twist phenomenon must lie within the layers themselves and not in their mutual orientations.

Some cases of twist are undoubtedly due to folding as is indicated by the outer layer in figure 45. This folding is possibly to be attributed to layer curvature for which, as we have already seen there is some evidence. However, this is by no means always the case. Many examples of crystals with twist boundaries are encountered

in which there is no visible evidence of folding. It is unlikely that the twist boundary in the crystal in figure 44, for example, can be attributed to layer folding. The most probable mode of formation of a twist boundary is that there is a slight change in lattice orientation at one of the step edges produced by the dislocation. As has already been pointed out, such changes are fairly common in paraffin layers. Visible evidence for this origin of twist boundaries is presented by figure 46 where an abrupt change in orientation can be seen in the basal sheet. In this way a twist boundary may be resolved into an ordinary grain or mosaic boundary combined with a screw dislocation.

Our results provide little evidence for Wilman's theory that the boundaries are produced by external stresses to which a crystal is subject during growth. If this theory were correct, one would expect the number of crystals with twist boundaries to be increased by crystallization before deposition. In this method the crystals are drawn up into a pipette from which they are transferred to the specimen mounts. They are consequently subjected to greater stresses than crystals prepared by the ordinary method, yet no increase in the number of crystals with twist boundaries are observed. Furthermore, if twist boundaries were produced by the method proposed by Wilman, one should expect to be able to detect a deformation of

the layer which forms the boundary between upper and lower growth patterns. Even when the twist angle is large, no such deformation is usually observed.

The reason why this effect appears to be more widespread in the ester than in the simple paraffins is not clear. Certainly, it has not been possible to get an overall estimate of the frequency of twist boundaries in the paraffins owing to the fact that the crystals seldom have growth patterns developed on both sides. This consideration will also apply to the Wilman work since the paraffin specimens were probably prepared by the same method as those used for the electron microscope study. Twist boundaries do, however, occur in the paraffins and the observation of them in crystals of paraffin mixtures has been reported earlier in this work. (Section IIIb). If, in fact, twist boundaries are more common in the esters than in the paraffins, this may be due to the presence of an oxygen link in the molecule. As Malkin (1933) has pointed out, there is evidence that this link is somewhate flexible. This may make the mutual rotation of two successive layers easier since the parts of the molecules nearest the twist boundaries may be able to adjust themselves to fit into the potential hollows of the underlying layer without alteration of the position of the rest of the molecules. Nevertheless it is difficult to explain the observation of

twist in the alcohols and iodides studied by Wilman on this basis.

An interesting consequence of the observations on ester crystals is that an apparent crystal discontinuity may, in fact, be penetrated by a screw dislocation. Thus Wilman derived his conclusion on the basis of a consideration of separate crystal sheets. The picture is, however, considerably altered by the realisation that these sheets are in fact a single sheet arranged in a helicoid structure.

f) TWIN GROWTH.

The results of the study of n-propyl n-pentacontanoate indicate that twinning occurs with great readiness in crystals of this compound. Twinning of comparable extent has hithertoo been observed in the long chain compounds n-hectane (Dawson, 1952) n-dooctacontane (Dawson and Duncan, unpublished) and n-pentacontanol (Dawson and Watson, unpublished), but no examples of it have been encountered in the pure paraffins n-hexatriacontane (Dawson and Vand, 1951) and n-nonatriacontane, although twinning has been observed in mixtures of these paraffins. The fact that twinning has been noted to occur in crystals in the stage before the formation of screw dislocations is significant. As a consequence it seems probable that twinning appears in the nucleation stage.

In a consideration of this question it must be borne in mind that the lattice of paraffin crystals is $\overset{a}{\Lambda}$ pseudo-hexagonal one, the deviations from a true hexagonal lattice arising from the absence of chain rotation. Under certain circumstances, however, where the chains require a high energy, chain rotation sets in and the lattice becomes hexagonal. This type of change in structure has already been reported by Müller (1932) for a series of paraffins near their melting points. In the crystal nucleus the

molecules also have a high energy and it is possible that the nucleus may also have a hexagonal structure. Twinning of the type which occurs in the paraffins across the diagonal is not possible in a hexagonal lattice since the twin is identical with the original lattice. As the size of the nucleus increases the energy of the molecules decreases and after reaching the critical dimensions, the nucleus must undergo a transition to the normal orthorhombic structure. In the hexagonal lattice this change can proceed along any one of the three closest-packed directions of a molecular layer. Consequently, if the nucleus is large enough different directions may be chosen in different parts of the nucleus and twinning may result. The liklihood of twinning will thus depend on the size of the crystal nucleus, the radius of which is given by

$$r_c = \frac{a\,\phi}{2k\,T \ln \alpha}$$

The size of the critical nucleus, and, if this interpretation is correct, the probability of twinning are consequently functions of temperature and supersaturation. Unfortunately, the present lack of data concerning supersaturation makes a quantitative verification of this theory impossible. Nevertheless, the qualitative results obtained in the study of paraffin derivatives are a positive indication that any satisfactory theory of twinning in these compounds must be based on these conditions. For example, the fact that

the size of the critical nucleus is dependent on temperature points to the possibilty of an explanation of the temperature relations observed by Dawson (1952) in n-hectane, where twinning was found to be favoured by a decrease in temperature. On the other hand, the supersaturation effect will depend on differences in solubility, which is, in turn, a function of the chain length. In this way it is possible to suggest a reason for the otherwise inexplicable difference in behaviour between the lower paraffins, n-hexatriacontane and n-nonatriacontane, and the very high ones, n-hectane and n- dooctacontane.

A further point emerges from the result indicated in section VIe, where it was pointed out that when two sheets of molecules are superposed the twinned orientation is second in stability to that of complete register. Consequently when a layer growing on top of another layer in which there is a twin boundary, crosses this boundary, it can either retain its orientation or twin correspondingly. The micrographs shown in figures 40 and 43 indicate that both processes do, in fact, occur. It will also be noted that, should twinning occur every time a fresh layer crosses the boundary, the boundary will assume a two dimensional character. Consequently the existence of a screw dislocation in a crystal can lead to an extension of a twin boundary.

g) THE EFFECTS OF IMPURITIES.

The effect of dust particles on the growth pattern has already been described in section IIIC (a) It is clear from the results obtained in the study of the long-chain paraffin derivatives that the influence of such impurities on the growth process is a purely secondary character. No evidence whatsoever has been forth-coming for the time-honoured belief in crystal nucleation by dust particles. Dust particles are rarely in evidence at the growth tip of a crystal, and even when they are, they show no characteristic effect.

Impurities of a molecular nature also seem to be without marked effect on crystal growth. Thus the results of the investigation of paraffin mixtures indicate that on the whole crystal growth is normal and show few distinctive features. Certain characteristics of paraffin crystallization, however, such as alteration in lattice orientation in crystal sheets and internal slip appear to be intensified. The ease with which dislocations are formed, would, from the complex growth centres observed, appear to be increased. These observations are probably to be attributed to the increased disorder resulting from the creation of holes in the polymethylene lattice. These holes are probably also responsible for a weakening of the interlayer bonding in

the crystals, and this may account for the occurrence of twist in these mixtures, which has hitherto not been encountered in the pure paraffins.

h) DIFFERENTIAL ETCHING PHENOMENA.

The observation that, in the crystals of stearic acid grown from benzene, two adjacent sets of {110} steps tend to be very irregular, is probably to be attributed to a feature of these steps pointed out by Verma and Reynolds (1953) in attempting to account for a similar phenomenon observed in their optical work. These authors point out that not all the {110} steps are equivalent since the unit cell is monoclinic. Consequently on one side of the crystal with respect to the b-axis the molecules in the exposed edges make an obtuse angle with terraces preceding them, while on the other the angle is acute. This feature is likely to have a profound influence on etching since where the edge makes an obtuse angle with the crystal face, the molecules will be dissolved more readily than where it makes an acute angle. The growth process will be similarly affected, since the addition of molecules to an edge making an acute angle with the crystal face will be considerable impeded. This is confirmed by the fact that the growth tip is frequently displaced to one side of the crystal as in figure 28.

The etching effect would seem to be connected with the method of preparation, since the crystals grown

from petroleum ether show the effect when prepared by the same method as the benzene crystals but not when prepared by the usual method. The most likely stages at which etching could occur is in the stripping onto a water surface or in the subsequent drying down. Thus the etching may be produced by some solution of the crystals in water during stripping, or alternatively by exposure to the water vapour during drying.

i) CRYSTALLINE MODIFICATIONS.

The crystalline modifications encountered in the specimens of n-nonatriacontane, stearic acid and n-hexadecane 1,16-dicarboxylic acid are those expected from the previous x-ray and electron diffraction investigations of these compounds. This is not the case however in the case of n-propyl pentacontanoate. The previous x-ray investigations of ester crystals cited in the Introduction would have led one to expect crystals with the monoclinic β-structure. Only one case of crystallization from solution in the orthorhombic form has been reported (Francis, Collins and Piper, 1937). This occurred in the case of ethyl n-tetratetracontanoate $C_{46}H_{92}O_2$, and since re-crystallization gave monoclinic crystals, this exception was attributed to impurities. The suggestion that impurities may be responsible for such variations in habit now seems improbable in view of the variations observed in the modification obtained in the case of stearic acid (see section IIIC (c) and also Stenhagen and von Sydow, 1953). Moreover there is little doubt as to the purity of the n-propyl n-pentacontanoate and this is confirmed by the fact that measurements of the interfacial angle of crystals of another ester, n-propyl n-nonahexacontanoate ($C_{72}H_{144}O_2$) prepared in the same way, showed that these were also orthorhombic.

The variations in crystalline modification observed in long chain compounds must consequently be due to factors other than purity. It has been argued by a number of authors (e.g. Coumoulos and Rideal, 1941) that in thin multi-layers of the long-chain paraffin derivatives the stable crystalline modifications may be different from those of the three-dimensional state. Thus while thick multi-layers (~1000 layers) are found to have the normal β-structure (Knott, Schulman and Wells, 1940), Coumoulos and Rideal find that thin multi-layers (<20 layers) are orthorhombic. Since the crystals suitable for electron microscopy are generally only a few molecular layers thick, this may also account for the fact that they assume the orthorhombic form. However, in the absence of further data on the crystalline form of three-dimensional n-propyl n-pentacontanoate crystals it is not possible to verify this conclusion.

A P P E N D I C E S.

These appendices contain the derivations of results, quoted in the text which for reasons of clarity have been omitted from the body of the thesis.

A. The distance between kinks in molecular sheets of paraffins.

It has been shown by Burton, Cabrera and Frank (1951) that the distance between kinks (X_o) in a molecular edge is given by

$$X_o = \tfrac{1}{2}a \quad \exp\left[\phi/kT\right]$$

where ϕ is the energy of interaction between nearest neighbours. This result has been derived for simple close-packed lattices, but should also be valid for the paraffin lattice when the latter is treated as approximately hexagonal close-packed. It will be appreciated from this expression that in order to find X_o we must first calculate ϕ.

n-Octadecane melts at 28°C and its heat of fusion 55 cals/gm. at this temperature may be added to the heat of evaporation 85 cals/gm. of the liquid paraffin extrapolated to 25°C to obtain an estimate of the heat of sublimation of the solid at 25°C. This gives a value of 140 cals/gm. This value remains very nearly constant for the higher paraffins and may therefore be regarded as an

approximate estimate for the heats of sublimation of paraffins at 25°C. For the paraffin $\underline{n}\text{-}C_{50}H_{102}$ the molar heat of sublimation is thus given by

$$L_s = M \times l_s = 702 \times 140 = 98300 \text{ cals/mole.}$$

where M = molecular weight and l_s = heat of sublimation in cals/gm. Consequently it follows that the molecular heat (ds) of sublimation is given by

$$\mathcal{A}_s = \frac{L_s}{N} = \frac{98300}{6 \times 10^{23}}$$

where N is Avogadro's number. Neglecting the energy of interaction between the terminal CH_3 - groups, the energy of interaction between neighbouring molecules is equal to 1/6th the molecular heat of sublimation, since each molecule has six nearest neighbours. Hence

$$\phi = \frac{98300}{36 \times 10^{23}}$$

It follows that at 27°C

$$\phi/kT = \frac{98300}{36 \times 10^{23}} / 0.33 \times 10^{23} \times 300$$

$$\simeq 27$$

Consequently

$$X_o = \tfrac{1}{2} a \exp\left\{\phi/kT\right\} \simeq \tfrac{1}{2} a \times 10^6$$

This result is anomalously high since it indicates that the

distance between kinks is as great as 0.01 cm. Furthermore increases in the length of the chain will give even greater results. Thus for $C_{100}H_{202}$ we would have

$$X_o = \tfrac{1}{2}a \times 10^{12}$$

It is therefore unlikely that the result derived by Burton, Cabrera and Frank can be properly applied to these compounds. Furthermore, the derivation of these authors is made on the basis of crystals growing from the vapor. While at first sight there would appear to be little difference in the case of the crystal growing from solution, since the expression only involves energies of interaction, it is probable that the solvent facilitates the transfer of molecules from the positions in the step to kink positions, and it may be more correct to use the heat of solution for the calculation. Nevertheless the result may be regarded as a qualitative indication that the distance between kinks in these compounds is rather large, compared with the same distance in simple substances. This is due to the molecular length of these compounds which will make the creation of kinks more difficult.

B. CALCULATION OF POSSIBLE TWIST ANGLES.

Figure 56 represent two superimposed layers of atoms. By rotating both layers about O in opposite directions through an angle $\delta/2$, the atoms at the points $\{u_1 v_1\}$ and $\{\bar{u}_1 \bar{v}_1\}$ can be made to coincide along the original a-axis direction. The angle $\delta/2$ is then given by

$$\tan \frac{\delta}{2} = \frac{v_1 \, b}{u_1 \, a}$$

Similarly there may simultaneously be a coincidence along the original b-axis direction of the points $\{u_2 v_2\}$ and $\{\bar{u}_2 v_2\}$. In this case $\delta/2$ will also be given by

$$\tan \frac{\delta}{2} = \frac{u_2 \, a}{v_2 \, b}$$

The condition for two such coincidences to occur simultaneously is

$$\frac{u_1 \, u_2}{v_1 \, v_2} = \frac{b^2}{a^2}$$

These results which have been derived by Wilman (1951) may be applied ot the case of the paraffin lattice in which $a = 7.40\text{Å}$ and $b = 4.95\text{Å}$. The condition for coincidences in two perpendicular directions then gives

$$\frac{u_1 \, u_2}{v_1 \, v_2} \simeq \frac{b^2}{a^2} = \frac{25}{55} = \frac{5}{11}$$

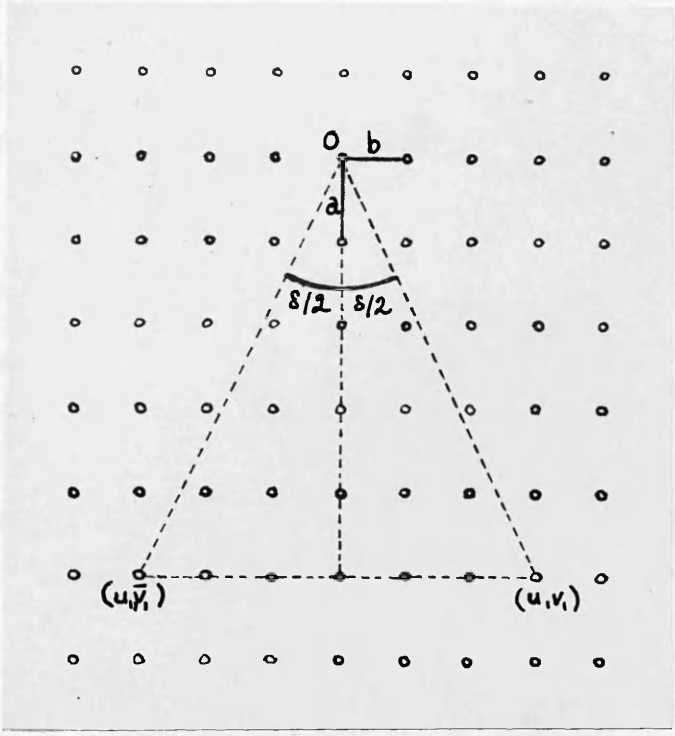


Figure 56.

i.e. the ratio of the product of the a-axis co-ordinates the product of the b-axis co-ordinates must be equal to 5/11. We must consequently choose values of u, u_2, v, v_2 which will give this ratio. We can thus take the following cases

1. $u_1 = 1 \qquad u_2 = 5$

$v_1 = 1 \qquad v_2 = 11$

This gives $\tan \frac{\delta}{2} = \frac{v_1 b}{u_1 a} = \frac{1 \times 4.95}{1 \times 7.40} = 0.668 \quad \therefore \frac{\delta}{2} = 33.8^\circ$

and $\tan \frac{\delta}{2} = \frac{u_2 a}{v_2 b} = \frac{5 \times 7.40}{11 \times 4.95} = 0.679 \quad \therefore \frac{\delta}{2} = 34.2$

Average value of $\frac{\delta}{2} = 34.0^\circ$

Hence angle of twist $= 68.0^\circ$

2.

This gives $\tan \frac{\delta}{2} = \frac{v_1 b}{u_1 a} = \frac{1 \times 4.95}{5 \times 7.40} = 0.134 \quad \frac{\delta}{2} = 7^\circ 38^1$

$\tan \frac{\delta}{2} = \frac{u_2 a}{v_2 b} = \frac{1 \times 7.40}{11 \times 4.95} = 0.136 \quad \frac{\delta}{2} = 7^\circ .45^1$

Hence angle of twist $= \delta = 15^\circ 23^1$

3. The condition is, of course also satisfied if $\frac{u_1\ u_2}{v_1\ v_2} = \frac{10}{22}$ consequently we may use the values:

$$u_1 = 10 \qquad u_2 = 1$$

$$v_1 = 1 \qquad v_2 = 22$$

This gives $\tan \frac{\delta}{2} = \frac{v_1 b}{u_1 a} = \frac{1 \times 4.95}{10 \times 7.40} = 0.668 \quad \therefore \frac{\delta}{2} = 3^\circ 49^1$

and $\tan \frac{\delta}{2} = \frac{u_2 a}{v_2 b} = \frac{1 \times 7.40}{22 \times 4.95} = 0.0678 \quad \therefore \frac{\delta}{2} = 3^\circ 58^1$

Hence the angle of twist $= \delta = 7^\circ 47^1$

4. Similarly we may put $\frac{u_1\ u_2}{v_1\ v_2} = \frac{15}{33}$ and take the co-ordinates as

$$u_1 = 5 \qquad u_2 = 1$$

$$v_1 = 1 \qquad v_2 = 11$$

This gives $\tan \frac{\delta}{2} = \frac{v_1 b}{u_1 a} = \frac{1 \times 4.95}{15 \times 7.40} = 0.0446 \quad \therefore \frac{\delta}{2} = 2^\circ 33^1$

and $\tan \frac{\delta}{2} = \frac{u_2 a}{v_2 b} = \frac{1 \times 7.40}{33 \times 4.95} = 0.0453 \quad \therefore \frac{\delta}{2} = 2^\circ 36^1$

Hence angle of twist $= 5^\circ 9^1$

It is obvious that we can obtain further angles by

multiplying the numerator and denominator by increasingly larger factors. However, as we do so the co-ordinates assume ever increasing values and the proportion of coincidences between the molecules in the two layers becomes correspondingly smaller.

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